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Physics. — *Magnetic resolution and nuclear moment of Rhenium.* By  
P. ZEEMAN, J. H. GISOLF and T. L. DE BRUIN.

(Communicated at the meeting of January 30, 1932.)

*Introduction.*

The first details concerning the optical spectrum of Rhenium were published by MEGGERS in a preliminary note<sup>1)</sup>. This note was followed by a complete description of the spectrum from 2500 Å to 8000 Å, while a beginning of the classification was made<sup>2)</sup>. In that article MEGGERS gives an elaborate review of the literature concerning the discovery and preparation of Rhenium, and of the work done upon the Röntgen spectra.

The absorption spectrum of Rhenium was obtained by us, by means of an underwater sparc between a pair of Rhenium electrodes, photographed with a HILGER  $E_1$  quartz spectrograph. It appears that the triplet:  $\lambda\lambda$  3452—3460—3465 gives strong absorption, and might therefore be considered as combinations with the ground level.

MEGERS has now identified these three lines as combinations of a  ${}^6P_{3/2, 7/2, 5/2}$  term with the groundterm  $(d^5 s^2) {}^6S_{5/2}$ .

We have investigated the hyperfine structure and the magnetic resolution of these strong lines. The results of this investigation have been published already in a short note in "Nature"<sup>3)</sup>.

A more complete description will be given now.

*The hyperfine structure of the groundtriplet of Rhenium.*

*Experimental details.* The photographs were made in the third order of a six inch grating with 15000 lines per inch and with a radius of curvature of 21 feet, in an Eagle mounting. The scale is 0.832 Å per millimeter.

The material used was powdered pure Rhenium, obtained from the "Chemische Werke, Leopoldshalle".

Some of this powder was brought upon the positive pole of a copper arc in vacuum. With a current of 5 ampères and 110 volts the Rhenium arc spectrum was extremely strong, so that exposures of about one minute were sufficient.

<sup>1)</sup> MEGGERS, Phys. Rev. 37, 219 (1931).

<sup>2)</sup> MEGGERS, Bureau of Standards Journal of Research 6, 1027 (1931).

<sup>3)</sup> P. ZEEMAN, J. H. GISOLF, T. L. DE BRUIN, Nature 128, 637 (1931).



Perutz Fliegerplatten were used for their very fine grain. By means of a ZEISS microphotometer which operates with a photocell, photograms were made from the photographs of the hyperfine structures.

The measurements were executed both on the original plates, and on the photograms. The results of these measurements differ very little. In the final dates the average is taken from the measurements on the plates and on the photograms.

*Theory and results.* The theory of hyperfine structure was first given by PAULI<sup>1)</sup> and has been described by several authors. A fairly complete review is given by PAULING and GOUDSMIT in their book "Structure of line spectra" chapter 11. It will therefore be sufficient to give a summing up of the facts which are necessary to give the interpretation of the patterns we have obtained.

To the nucleus is ascribed a spin moment  $I \cdot h/2\pi$ , in which  $I$  is a new quantum number. This moment is composed with the mechanical moment  $J$  of the extranuclear electrons to a resulting total moment vector  $F$ . This vector will have the value  $F \cdot h/2\pi$ , in which  $F$  is called the hyperfine structure quantum number.

An electron configuration with a mechanical moment  $J$  (an "electron state") will give rise to either  $2I + 1$  hyperfine structure terms with hyperfine structure quantum numbers  $F = J + I; J + I - 1; \dots; J - I$ , or to  $2J + 1$  terms with quantum numbers  $F = I + J; I + J - 1; \dots; I - J$ , according to whether  $I$  or  $J$  is the smaller of the two. Therefore it is possible to deduce the value of the nuclear moment from the number of hyperfine structure terms that belong to one electron state, provided that the  $J$  value of the considered electron state is known.

The energy difference between two hyperfine structure terms with quantum numbers  $F$  and  $F - 1$ , belonging to one electron state, is given by the product of the quantum number  $F$  and a quantity  $A$  called the "interval constant", having the same value for all the hyperfine structure terms that belong to one electron state. (Interval rule.)

Thus the value of the quantum number  $F$  can be determined from the mutual position of the hyperfine structure terms and when the quantum number  $J$  is known, one may obtain the value of the nuclear spin  $I$ .

The combination of two hyperfine structure terms to a spectral line is subjected to the exclusion rules:  $\Delta F = 0, \pm 1$  and  $\Delta J = 0, \pm 1$ , while the combinations  $J = 0$  to  $J = 0$  and  $F = 0$  to  $F = 0$  are forbidden.

The combinations of the hyperfine structure terms of two electron states form together a hypermultiplet. In such a hypermultiplet the strongest components will come from transitions by which  $\Delta J$  and  $\Delta F$  have the same sign and the intensity of these components will be ranged according to the  $F$  values of the initial terms.

<sup>1)</sup> W. PAULI, Naturwiss. 12, 741 (1924).

The value of the interval constant  $A$  may be very different for the various electron states of an atom.

The hypermultiplet that arises from the transition of one electron state to another, will have a very regular shape if one of the two electron states has an interval constant that is vanishing small. In this case the hypermultiplet consists of a number of lines of gradually decreasing intensity and space for which the same interval rule holds as far the terms itself.

We found that in Rhenium the hypermultiplets  $\lambda$  3452  ${}^6S_{5/2} - {}^6P_{5/2}$ ,  $\lambda$  3460  ${}^6S_{5/2} - {}^6P_{7/2}$ ,  $\lambda$  3465  ${}^6S_{5/2} - {}^6P_{3/2}$ , are quite of this type and the measurements make it certain that it is the common electron state  $d^5 s^2 {}^6S_{5/2}$  that is practically simple.

The structures consist of respectively four, six and five components all three with the intensity and space decreasing to longer wavelength.

The measurements gave the following results:

$\lambda$  3452  ${}^6S_{5/2} - {}^6P_{5/2}$  (Fig. 4)

$$\begin{aligned}\Delta\lambda &= 0 + 0.064 + 0.111 + 0.140 \dots \text{\AA} \\ \Delta\nu &= 0 - 0.54 - 0.94 - 1.17 \dots \text{c.m.}^{-1}\end{aligned}$$

the accuracy for the first three components being about two units.

The interval ratios are: 4.0:2.9:1.8.

This gives for the hyperfine structure quantum numbers  $F$  the values 4, 3, 2 and 1.

It follows that  $I = 5/2$ .

The interval constant amounts to  $0.134 \text{ cm}^{-1}$  calculated from the first two intervals.

$\lambda$  = 3460  ${}^6S_{5/2} - {}^6P_{7/2}$  (Fig. 2)

$$\begin{aligned}\Delta\lambda &= 0 + 0.070 + 0.127 + 0.170 + 0.201 + 0.224 \dots \text{\AA} \\ \Delta\nu &= 0 - 0.58 - 1.06 - 1.41 - 1.68 - 1.87 \dots \text{c.m.}^{-1}\end{aligned}$$

For the first two components the error in the measurements in less than one unit. For the following two it may be about two units.

The interval ratio is: 6.0:4.0:3.7:2.7:2.0. Thus the  ${}^6P_{7/2}$  state has six hyperfine structure terms with quantum numbers: 6, 5, 4, 2, 1.

This gives again  $I = 5/2$ .

The interval constant calculated from the first two intervals is  $0.096 \text{ c.m.}^{-1}$

$\lambda$  = 3465  ${}^6S_{5/2} - {}^6P_{3/2}$  (Fig. 3)

$$\begin{aligned}\Delta\lambda &= 0 + 0.062 + 0.115 + 0.156 + 0.185 \dots \text{\AA} \\ \Delta\nu &= 0 - 0.52 - 0.96 - 1.30 - 1.54 \dots \text{c.m.}^{-1}\end{aligned}$$

For the first three components the error in the measurements will not exceed two units.

The interval ratio is: 5.0:4.2:3.3:2.4.



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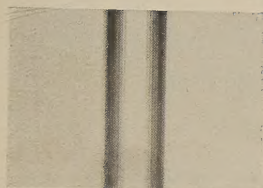


Fig. 1

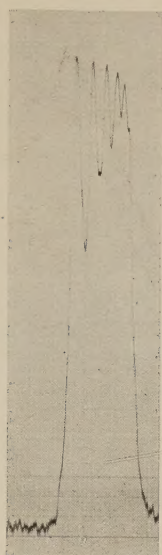


Fig. 2

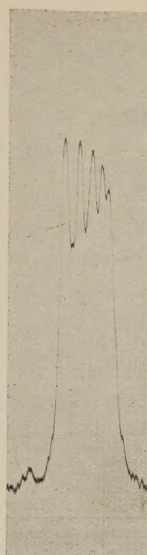


Fig. 3

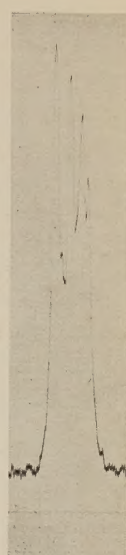


Fig. 4



Fig. 5

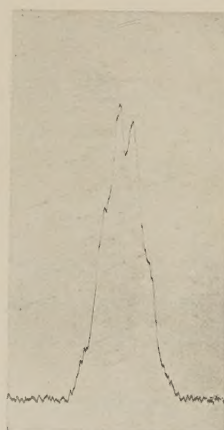


Fig. 6

*Re  $\lambda$  3460.*

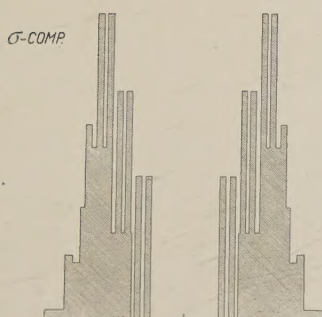


Fig. 5a

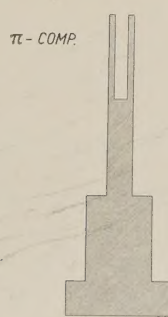
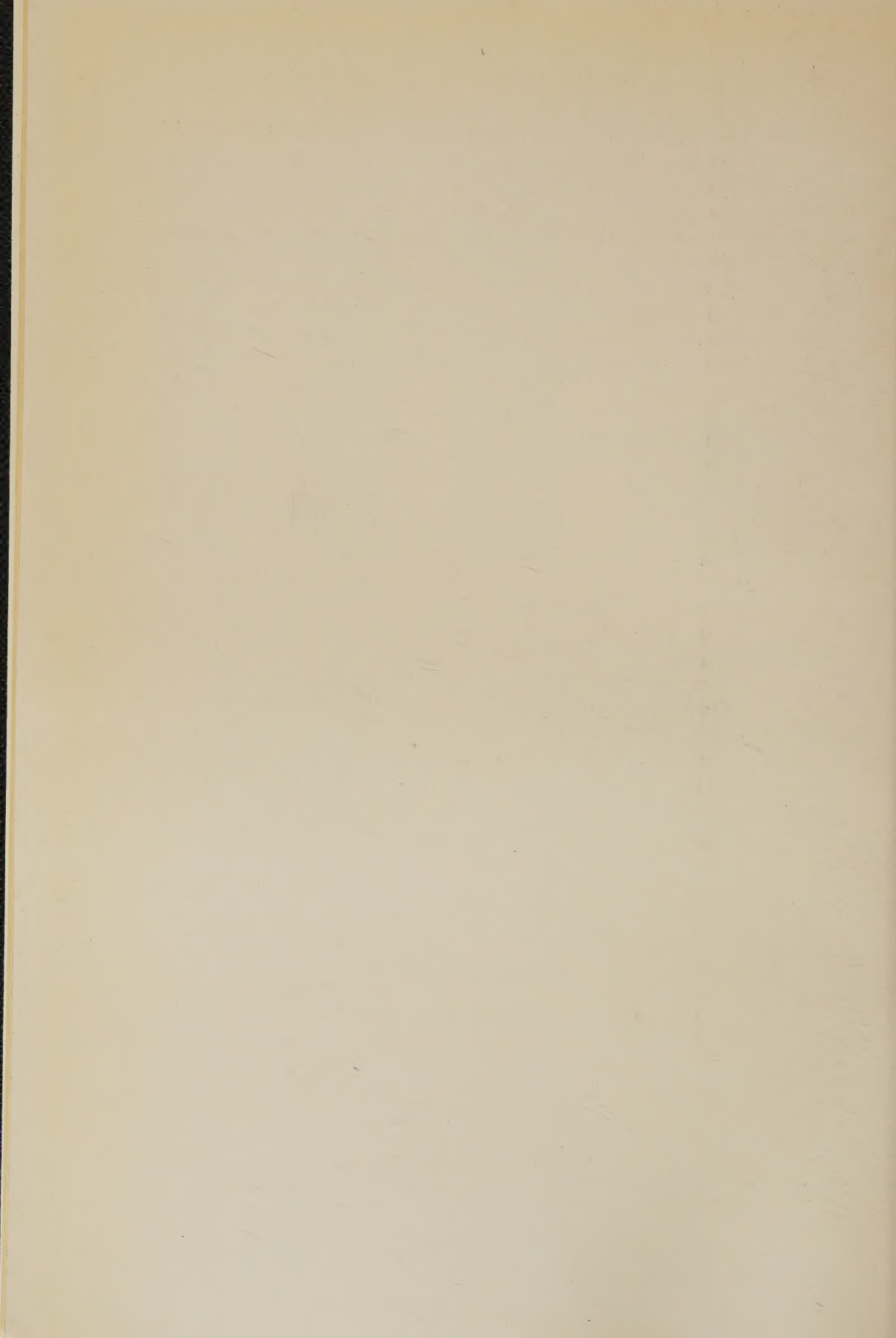


Fig. 6a



In this case a faint sixth component must be present, but it cannot be expected to be resolved.

Here too we get perfect agreement for a nuclear moment  $I = 5/2$ .

The first two intervals give an  $A$  value of 0.107 c.m.<sup>-1</sup>

So we can say that the nuclear moment has proved to be  $5/2 \cdot h/2\pi$  as was suspected already by GREMMER and RITSCHL<sup>1)</sup>

Meanwhile a short note has appeared of MEGGERS, KING and BACHER<sup>2)</sup>, in which the same conclusion is expressed.

It must be noticed that Rhenium has two isotopes 185 and 187 in ratio 1.62 to 1. The structure of the multiplets makes it certain that both the isotopes have the same nuclear moment and that the difference of the interval constants, or the isotope displacement, if present, must be very small. In this time the same lines are under investigation with apparatuses of higher resolving power.

### *Magnetic resolution.*

*Experimental details.* For this investigation is used the large WEISS electromagnet of this laboratory. A description can be found in an article by P. ZEEMAN and T. L. DE BRUIN<sup>3)</sup>.

The endplanes of the conical polepieces have a diameter of one centimeter. With a distance of these planes of about 4 m.m. and a current of 100 A. the fieldstrength amounts to 38900 Gauss.

As a lightsource was used a vacuum trembler of BACK<sup>4)</sup>. For this trembler it is necessary to have the material in the form of small bars, about two centimeters long, two millimeters broad and one millimeter thick. As the industry could not supply the Rhenium in the form of compact metal, we had to make our own electrodes.

The melting point of Rhenium being extremely high (3400°), this gave some trouble, but at least we succeeded in manufacturing bars of the desired dimensions, of quite pure and compact Rhenium, by melting the powder in the positive crater of a carbon arc.

The same bars were used as electrodes for the underwater spark in the investigation of the absorption spectrum that was mentioned at the beginning of this article.

The interrupted arc burned in air of 4 c.m. pressure with a current-strength of 2 Ampères and a tension of 110 Volts. Under these conditions the arc spectrum was very intense.

The optical arrangement was the same as in the experiments without magnetic field. The two states of polarisation were separated by means

1) GREMMER and RITSCHL. Zeitschr. für Instrumentenkunde 51 170 (1931).

2) MEGGERS, KING and BACHER. Phys. Review 38 1259 (1931).

3) P. ZEEMAN and T. L. DE BRUIN. Handbuch der physikalische Optik Bd. II. Gehrcke pag. 602.

4) See BACK—LANDÉ „ZEEMAN-effekt und Multiplettstruktur“ pag. 124.



of a calcspar rhomb. The time of exposure was varied from a half to three hours. The temperature of the grating was kept constant to  $0.01^\circ \text{C}$ . by using the principle: First regulate the room temperature to  $0.1^\circ$  and then regulate the grating temperature by a second step. This procedure first described in the article of ZEEMAN and DE BRUIN (Handbuch der phys. Optik, Gehrcke, Vol. 2, pag. 605, 1927) has been used with success by various physicists, with or without acknowledgment.

Again Perutz Fliegerplatten were used.

The measurements were made again both on the original plates and on the photograms.

*Theory and results.* The influence of the nuclear moment upon the magnetic resolution of the spectral lines was first found by BACK and GOUDSMIT<sup>1)</sup> for the Bismuth line  $\lambda$  4722, and they could show that their very beautiful resolution patterns were in perfect agreement with PAULI's suggestion. For the theory of the ZEEMAN effect of the hyperfine structure we may refer to the book of PAULING and GOUDSMIT cited before. We will mention only the following facts.

In an external magnetic field, each electron state is split up in  $2J + 1$  "magnetic" states characterised by magnetic quantum numbers  $m_j$  which are equal to  $J, J - 1, \dots, -J$ .

The energy differences between the successive magnetic states are equal, and are given by the product  $g.o.H$ . This is the ordinary magnetic resolution.

When there exists a nuclear moment, each of the  $2J + 1$  magnetic electron states gives rise to  $2I + 1$  equidistant magnetic hyperfine structure terms, with magnetic hyperfine structure quantum numbers  $m_i = I, I - 1, \dots, -I$ , provided the field is very strong.

The distance of the magnetic hyperfine structure terms that belong to one magnetic electron state with quantum number  $m_j$ , is given by the product of  $m_j$  and the interval constant  $A$  of that electron state.

At the transition of one electron state to another in such a very strong field, the magnetic quantum number  $m_i$  is not allowed to change. This makes that the nuclear moment causes a splitting up of each ordinary ZEEMAN component in  $2I + 1$  equidistant hyperfine structure components of equal intensity.

The distance between these hyperfine structure components which belong to the combination of two magnetic electron states with quantum number  $m_j$  and  $m'_j$ , and with interval constants  $A$  and  $A'$ , is given by  $m_j A - m'_j A'$ .

We have seen that in the case of Rhenium, the common term  $^6S_{5/2}$  of the triplet has an interval constant which is practically zero, and therefore in this case the distance of the  $2I + 1$  hyperfine structure components of

<sup>1)</sup> BACK and GOUDSMIT. Zeitschr. für Physik 47, 174, (1928).

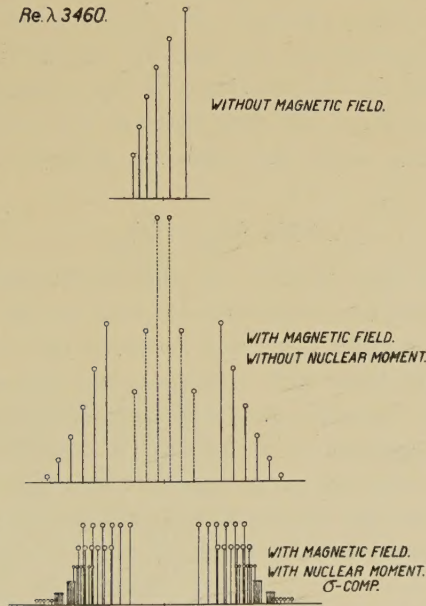


each ZEEMAN component is given by the product of the magnetic quantum number  $m_j$  and the interval constant  $A$  of the initial state.

The number of components in the magnetic resolution pattern may become extremely large when there is a nuclear moment, but most of these components won't be resolved in consequence of their very small mutual distance. Only for the ZEEMAN components which belong to the highest magnetic quantum numbers  $m_j$  it will be possible to resolve them each in their  $2I + 1$  hyperfine structure components. The most favorable case is therefor found in the line  $\lambda 3460$   ${}^6S_{5/2} - {}^6P_{7/2}$  for the transition  $m_j = 7/2$  to  $m_j = 5/2$ :

$$\lambda 3460 \quad {}^6S_{5/2} - {}^6P_{7/2}.$$

In the following figure is given the magnetic resolution of this line without nuclear moment, and the resolution pattern for a nuclear moment  $5/2 \cdot h/2\pi$  and an interval constant  $A = 0.096 \text{ c.m.}^{-1}$



In the photograph of the  $\sigma$ -components (fig. 1) the inner six components can be recognized immediately.

For the mean distance of these components is measured the value  $0.334 \text{ c.m.}^{-1}$ . This distance must be  $7/2 A$ . So we find for  $A$  the value  $0.095 \text{ c.m.}^{-1}$ , while the value of  $A$  found from the hyperfine structure without magnetic field is  $0.096 \text{ c.m.}^{-1}$ . The center of the group of six hyperfine structure components gives the place of the first ZEEMAN component when no nuclear moment is present.

From the place of this centre, we calculate for the LANDÉ splitting factor  $g$ , of the  ${}^6P_{7/2}$  state the value 1.76, while the LANDÉ formula gives the

value 1.714. However, from the structure of the  ${}^6P$  state it is obvious that the coupling deviates strongly from the RUSSELL—SAUNDERS type and so one need not wonder that a slight anomalous  $g$ -value is found. We have assumed that the  ${}^6S_{5/2}$  state has its normal  $g$ -value:  $g=2.000$ , this being probable in connection with the  $g$ -sum rule. The observed positions of the six subcomponents of the strongest  $\sigma$ -components and the positions calculated with  $g=1.76$  and  $A=0.096$  c.m. $^{-1}$  are given below.

Obs:	+2,91	+2,62	+2,24	+1,95	+1,60	+1,25	... c.m. $^{-1}$
Calc.:	+2,94	+2,60	+2,26	+1,93	+1,59	+1,26	... c.m. $^{-1}$
Obs:	-2,90	-2,60	-2,28	-1,93	-1,61	-1,24	... c.m. $^{-1}$
Calc.:	-2,94	-2,60	-2,26	-1,93	-1,59	-1,26	... c.m. $^{-1}$

The small deviations may be sufficiently explained by the overlapping of the non resolved groups of hyperfine structure components of the other components, as is seen in the preceding figure.

None of the other ZEEMAN components can be resolved in their sub-components. Representing groups of non resolved components by rectangles, we have constructed the intensity distribution as predicted by the theory (fig. 5a and 6a). Comparing with the photograms (fig. 5 and 6) the agreement is excellent. The two pikes at the outer side of each of the  $\sigma$ -groups originate from the magnetic quantum numbers  $m_j = 1/2$  and  $m_j = -1/2$ .

$$\lambda 3465 \text{ } {}^6S_{5/2} - {}^6P_{5/2}.$$

This line is much less suitable for the observation of the magnetic resolution of the hyperfine structure, because of the smaller  $m_j$  values and because of the smaller difference between the  $g$ -values of the two electron states. At the inner side of the  $\sigma$ -group and at the outer side of the  $\pi$ -group traces of hyperfine structure components can be seen.

Comparing the photogram of the resolution pattern (fig. 7 and 8) with the type calculated with the normal  $g$ -value and the  $A$  of the hyperfine structure without field (fig. 7a and 8a) the agreement is very satisfactory, though the  $g$ -value is probably not quite normal.

$$\lambda 3452 \text{ } {}^6S_{5/2} - {}^6P_{5/2}.$$

The calculated intensity distribution (fig. 9a and 10a) agrees with the observed type (fig. 9 and 10). In consequence of the small  $m_j$  values we cannot expect to resolve any of the hyperfine structure components.

In connection with a small asymmetry of the intensities as is seen from the photograms one is forced to consider whether the magnetic field can be called "very strong".

GOUDSMIT and BACHER<sup>1)</sup> have adapted the calculations of DARWIN<sup>2)</sup>

<sup>1)</sup> GOUDSMIT and BACHER, Zeitschr. für Physik 66, 13 (1930).

<sup>2)</sup> C. G. DARWIN. Proc. Roy. Soc. (A) 115, 1 (1927).



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Fig. 7

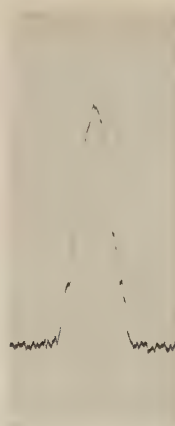


Fig. 8

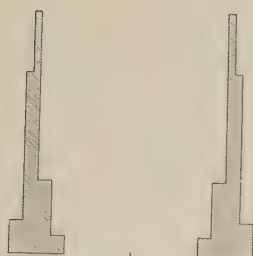


Fig. 7a



Fig. 8a



Fig. 9



Fig. 10



Fig. 9a

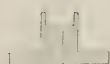


Fig. 10a





for the ordinary PASCHEN—BACK effect to the magnetic resolution of the hyperfine structure.

As a second order approximation the energy of a magnetic hyperfine structure state with quantum number  $m_i$ , which belongs to a magnetic electron state with quantum number  $m_j$  is given by:

$$E(m_i, m_j) = m_j g(j) \circ H + A m_i m_j + \frac{A}{2g(j) \circ H} [m_j \{I(I+1) - m_i^2\} - m_j \{J(J+1) - m_j^2\}]$$

In the preceding pages we have considered only the first two terms of the energy. When the third term is so small that it can be neglected, the field will be "very strong".

We have calculated the influence of this third term for the different transitions. These corrections are however smaller than the displacements of the intensity maxima due to the overlapping of several components and so we have not further considered them.

Resuming we can say that both the natural hyperfine structure and the magnetic resolution give independently for the nuclear moment of both the Rhenium isotopes the value  $I = 5/2$ .

*Laboratory "Physica" Amsterdam.*

#### DESCRIPTION OF THE PLATES

- Fig. 1. Resolution pattern of Rhenium  $\lambda 3460$  ( $\sigma$ -components). Enlargement 8 times. At each side of the centre the six subcomponents belonging to the strongest ZEEMAN components can be seen. The distance between these hyperfine structure components is  $0,04 \text{ \AA}$ .
- Fig. 2. Zeiss photogram of the same line  $\lambda 3460$  without magnetic field. The total breadth is  $0,224 \text{ \AA}$ .
- Fig. 3.  $\lambda 3465$  without magnetic field. Total breadth  $0,185 \text{ \AA}$ .
- Fig. 4.  $\lambda 3452$  without magnetic field. Total breadth  $0,140 \text{ \AA}$ .
- Fig. 5. This is a photogram of the same magnetic resolution pattern of which an enlargement is shown in fig. 1. The inner six components at each side of the centre are the hyperfine structure components belonging to  $m_j = 7/2$ . The outer two components at each side are non resolved groups belonging to  $m_j = +1/2$  and to  $m_j = -1/2$ .
- Fig. 5a. In this figure we have constructed the intensity distribution, representing non resolved groups by rectangles.
- Fig. 6 and Fig. 6a. Observed and calculated photogram of the  $\pi$ -components of the same line  $\lambda 3460$ . Non of the groups of hyperfine structure components are resolved.
- Fig. 7 and Fig. 8.  $\lambda 3465$   $\sigma$ - and  $\pi$ -components.
- Fig. 7a and Fig. 8a. Calculated types for  $\lambda 3465$   $\sigma$ - respectively  $\pi$ -components.
- Fig. 9 and 10.  $\lambda 3452$   $\sigma$ - and  $\pi$ -components.
- Fig. 9a and Fig. 10a. Calculated types for  $\lambda 3452$   $\sigma$ - respectively  $\pi$ -components.

The figures 7a to 10a are calculated with normal  $g$ -values. The  $g$ -values however may be a little anomalous, but they could not be deduced from the resolution patterns with sufficient accuracy.

**Physics.** — *Establishment of an Absolute Scale for the Thermo-electric Force.* By G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. Supplement N<sup>o</sup>. 69*b* to the Communications from the Physical Laboratory at Leiden.

(Communicated at the meeting of January 30, 1932.)

The results obtained for the thermo-electric forces of *Pb* and *Sn* at liquid helium temperatures and higher<sup>1)</sup> together with the assumption made probable by those results, that the THOMSON-heat  $\sigma$  is zero in the supraconducting state<sup>2)</sup>, render the establishment of an absolute scale for thermo-electric forces possible.

The THOMSON theory gives the formula

$$\frac{de}{dT} = \frac{\sigma_1}{T} - \frac{\sigma_2}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which on account of the NERNST theorem gives by integration

$$e = \int_a^T \frac{\sigma_1}{T} dT - \int_a^T \frac{\sigma_2}{T} dT \dots \dots \dots (2)$$

The integrals may be called the absolute thermo-electric forces per degree for each of the two metals, and they are of course of more interest than the thermo-electric force of the couple.

It is obvious from (2) that if the integral is known for one metal, it may be determined for any other metal at any temperature by measurement of the thermo-electric force against the first. To get the value of the integral for that one metal, it is, however, necessary to know the values of  $\sigma/T$  continuously from  $T$  down to the lowest temperatures. Fortunately the measurements seem to give such a knowledge with a fairly good degree of accuracy.

Below the critical point of *Sn* at 3.72° K  $\sigma/T$  is by assumption zero for *Sn* as well as for *Pb*. From 3.72 to 7.2° K it is zero for *Pb*, and may be calculated for *Sn* and for the special silver alloy wire called "normal" in the Communication mentioned<sup>3)</sup> by the aid of equation (1) from the thermoelectric forces against *Pb*. Above 20° K  $\sigma/T$  is known for the normal from the direct measurements of the THOMSON heat made by BORELIUS, KEESOM and JOHANSSON<sup>4)</sup> and may be calculated for *Pb* and *Sn* from the measurements of Comm. No. 217c. All these values have been determined graphically

<sup>1)</sup> G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. These Proc. **34**, 1365, 1931. Comm. Leiden N<sup>o</sup>. 217c.

2) Cf. § 3 Comm. Leiden N<sup>o</sup>. 217c.

3) Cf. Comm. Leiden N<sup>o</sup>. 217c § 1.

<sup>4)</sup> These Proceedings 31, 1046, 1928. Comm. Leiden N<sup>o</sup>. 196a.



and are shown in Fig. 1 by the full lines. Between 7.2 and 20° K there is an interval, where no values could be directly calculated from our measurement. As will be seen from the diagram in the case of *Sn* the gap can, however, quite easily be filled up by connecting the curves on its sides. As to *Pb* and the normal the shape of the curves between 7.2 and 20° is rather unfit for a graphical interpolation. The dotted lines in the figure were derived from the thermo-electric forces against *Sn* according to equation (1). At the critical points the curves are simply drawn as if there were a discontinuity in  $de/dT$ , though in fact we only know, that there is a rapid change. As however the curves are obtained here by graphical derivation this detail will have no influence on the result of the

TABLE I.  
Numerical values to Fig. 1.

°K.	$\frac{\sigma}{T}$ 10 <sup>8</sup> volt per (degree) <sup>2</sup>		
	Sn <sub>31</sub>	Pb <sub>31</sub>	Normal
<3.7	0	0	—
3.7	—1.7	0	+0.1
5	1.9	0	0.1
6	2.3	0	0.2
7	2.55	0	0.2
7.2	—	—14.3	0.2
10	3.3	15.0	1.45
12.5	3.7 <sub>5</sub>	4.2	3.5
15	4.0	0.6	3.5 <sub>5</sub>
17.5	4.0	0.3	2.17
20	3.8	0.37	1.55
30	2.9	+0.18	0.80
40	2.15	—0.04	0.25
50	0.86	0.09	—0.04
60	0.51	0.05	—0.03
70	0.44	0.13	+0.03
80	0.36	0.15	0.10
90	0.24 <sub>5</sub>	0.38 <sub>5</sub>	0.15 <sub>5</sub>
100	0.19	—	0.21

graphical integration in the following. The numerical values connected with Fig. 1 have been collected in Table I.

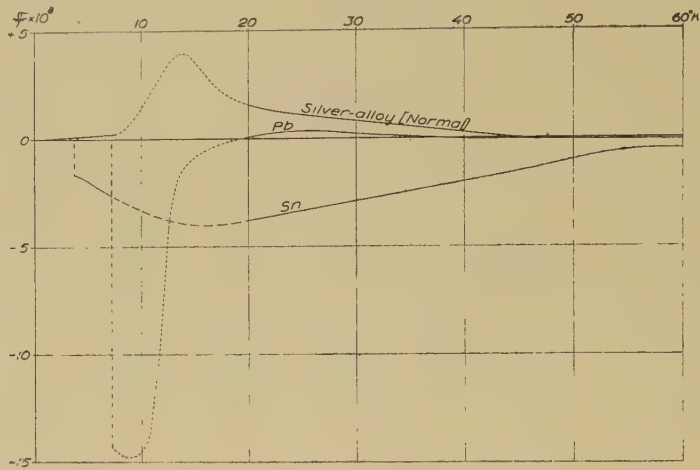


Fig. 1.  $\frac{\sigma}{T} = \frac{de_{abs}}{dT}$  for  $Sn_{31}$ ,  $Pb_{31}$  and silveralloy-normal in volt per  $(\text{degree})^2$ .

The curves in Fig. 1 have been graphically integrated, and the absolute thermo-electric forces per degree

$$e_{abs} = \int_0^T \frac{\sigma}{T} dT \quad . . . . . (3)$$

thus obtained are given in Fig. 2 and Table II. The even form of these curves as compared with the curves in Fig. 2 of Comm. N<sup>o</sup>. 217c, seems to confirm the correctness of the graphical interpolation for  $Sn$  between 7.2 and 20° K and also demonstrate the usefulness of the absolute scale.

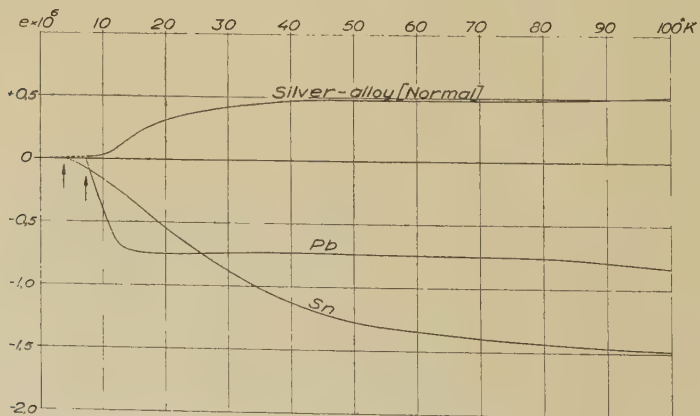


Fig. 2. Thermo-electric force in volt per degree for  $Sn_{31}$ ,  $Pb_{31}$  and silveralloy-normal in the absolute thermo-electric scale.



TABLE II.

Thermoelectric forces in microvolt per degree in the absolute thermo-electric scale.

$$\left( e_{abs} = \int_0^T \frac{\sigma}{T} dT \right)$$

°K	Sn <sub>31</sub>	Pb <sub>31</sub>	Normal
<3.7	0	0	+0.01
3.7	0	0	0.01
5	-0.023	0	0.01
6	0.042	0	0.01
7	0.067	0	0.01
7.2	0.073	0	0.01 <sub>5</sub>
10	0.15 <sub>5</sub>	-0.40	0.030
12.5	0.25	0.68 <sub>5</sub>	0.096
15	0.34 <sub>5</sub>	0.73 <sub>5</sub>	0.185
17.5	0.44 <sub>5</sub>	0.74	0.26
20	0.54 <sub>5</sub>	0.75	0.30 <sub>5</sub>
30	0.88 <sub>5</sub>	0.74	0.42
40	1.13	0.73	0.47 <sub>5</sub>
50	1.28 <sub>5</sub>	0.74	0.48
60	1.34	0.74 <sub>5</sub>	0.47 <sub>5</sub>
70	1.39	0.75	0.47 <sub>5</sub>
80	1.44	0.76	0.48
90	1.46 <sub>5</sub>	0.79 <sub>5</sub>	0.49 <sub>5</sub>
100	1.48 <sub>5</sub>	0.83 <sub>5</sub>	0.51 <sub>5</sub>

With further use of the measurements of BORELIUS, KEESOM and JOHANSSON on the THOMSON heat of the normal the  $e_{abs}$  of this wire are calculated further up to 300° K and are given in table III for the same temperatures as are used in our interpolated tables for thermo-electric forces per degree in the earlier papers<sup>1)</sup>. We estimate the error in these absolute thermo-electric forces at room temperature at about  $\pm 0.1$  micro-volt per degree.

<sup>1)</sup> These Proceedings 33, 17 and 32, 1930. Comm. Leiden N°. 206a and b.

TABLE III.

Thermo-electric force in microvolt per degree for the silveralloy-normal in the absolute thermo-electric scale.

$$\left( e_{abs} = \int_0^T \frac{\sigma}{T} dT \right)$$

°K	°C	$e_{abs}$	°K	°C	$e_{abs}$
2	-271.1	+0.00 <sub>5</sub>	73.1	-200	0.48
4	269.1	0.01	83.1	190	0.49
6	267.1	0.01	93.1	180	0.50
8	265.1	0.01 <sub>5</sub>	103.1	170	0.52
10	263.1	0.03	113.1	160	0.54
13.1	260	0.12	133.1	140	0.61
18.1	255	0.27	153.1	120	0.68
23.1	250	0.35 <sub>5</sub>	173.1	100	0.76
28.1	245	0.40 <sub>5</sub>	193.1	80	0.84 <sub>5</sub>
33.1	240	0.44	213.1	60	0.93
38.1	235	0.46 <sub>5</sub>	233.1	40	1.02
43.1	230	0.48	253.1	20	1.11
53.1	220	0.48	273.1	0	1.20
63.1	210	0.48	293.1	+20	1.29 <sub>5</sub>

We at last wish to point out that the possibility of using the measurements on the supraconductors for the establishment of the absolute scale was not quite clear to us at the time as the measurements were performed. The results are therefore not in details the most convenient for this purpose. It is probable that the scale can be more exactly determined by measurements on an extended number of supraconductors.

#### Summary.

The authors introduce  $e_{abs} = \int_0^T \frac{\sigma}{T} dT$  ( $\sigma$  = THOMSON-heat) as the

thermo-electric force per degree of a metal in the absolute thermo-electric scale. They calculate this quantity for tin, lead, and the silveralloy-normal they used, on the basis of their measurements of the thermo-electric forces and of the THOMSON-heat, of the assumption that  $\sigma=0$  in the supraconducting state, and of an interpolation for tin between 7.2 and 20° K.



**Physics.** — *Measurements on Thermo-Electric Forces down to Temperatures Obtainable with Liquid or Solid Hydrogen.* By G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. (Communication N<sup>o</sup>. 217d from the Physical Laboratory at Leiden.)

(Communicated at the meeting of January 30, 1932.)

§ 1. *Introduction.* While preparing and performing our measurements on thermo-electric forces down to liquid helium temperatures we had an opportunity to collect a number of data on thermoelectric forces at temperatures obtainable with liquid or solid hydrogen. We give these data in this paper for those metals or alloys for which we did not get numbers at liquid helium temperatures.

The apparatus used and the method followed were the same as described in our preceding paper on measurements at liquid helium temperatures<sup>1)</sup>.

§ 2. *Results for Ag and for an alloy of Ag with Au.* The silver was supplied for spectroscopic purposes by HILGER in London. The spectroscopical analysis had given small traces of Ca as the only considerable impurity. As a matter of fact we tried to investigate this silver also at the liquid helium temperatures. We got however no good measurements on it at those temperatures. The results for the thermo-electric force per degree, obtained when the coldest junction was at the boiling point of helium, was not in harmony with those, obtained with the coldest junction at the temperature of solid hydrogen. The reason may be, that, on account of the great heat conductivity, which is to be expected for such a pure silver at the temperature of liquid helium, a considerable part of the temperature difference takes place at the junctions. It may be necessary to use long and thin wires in such measurements. Though we thus cannot give any numerical values for the thermo-electric forces below 10° K., it is to be noted that they were found to be positive against our normal, which was an alloy of Ag with 0.37 at. % Au. The results for temperatures above 10° K are given in table I.

We have also measured another alloy of Ag with 0.91 at. % Au. As might be expected it falls on the other (negative) side of the normal than the pure Ag does. In this figure for comparison the curve for a wire of silver got from KAHLBAUM and measured in 1929<sup>2)</sup> (here marked Ag<sub>29</sub>) is also again traced. This silver seems to contain some thermo-electrically rather active impurity.

<sup>1)</sup> These Proceedings 34, 1365, 1931. Comm. Leiden N<sup>o</sup>. 217c.

<sup>2)</sup> These Proceedings, 33, 17, 1930. Comm. Leiden N<sup>o</sup>. 206a.

TABLE I.

Thermo-electric force in microvolt per degree for pure and alloyed Ag against silveralloy-normal.					
Ag <sub>31</sub> (HILGER)				Ag + 0.91 at. % Au	
°K.	e	°K.	e	°K.	e
10.1	+0.19	42.5	+0.73	17.3	-0.15
12.0	0.22	42.7	0.66	17.3	0.16
13.7	0.24	47.2	0.68	23.9	0.20
15.8	0.22	48.0	0.66	30.4	0.25
17.3	0.34	58.9	0.51	36.8	0.27
19.4	0.35	67.9	0.45	42.8	0.33
24.0	0.57	78.9	0.37	48.0	0.33
26.7	0.55	86.3	0.32	59.3	0.32
30.3	0.70	94.2	0.30	68.3	0.33
36.5	0.71	102.7	0.28	77.3	0.33
36.7	0.74	275.4	0.21	85.9	0.33
				94.0	0.35
				102.2	0.35
				275.3	0.38

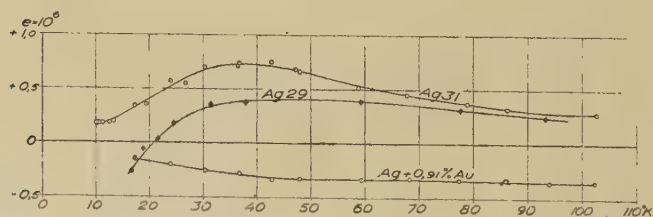


Fig. 1. Thermo-electric force in volt per degree. Against silveralloy-normal.

In Fig. 2 we have also given the thermo-electric force per degree for pure and alloyed silver on the absolute scale<sup>1)</sup>. The influence of the added gold appears here more clearly. It seems rather probable that the pure silver approaches zero from the positive side of the axis in the absolute thermo-electric scale. However the measurements have not yet

<sup>1)</sup> Cf. These Proceedings, 35, p. 10, 1932. Comm. Leiden Suppl. N<sup>o</sup>. 69b.

given any clear knowledge of the thermo-electric properties of pure not supra-conductive metals at the lowest temperatures.

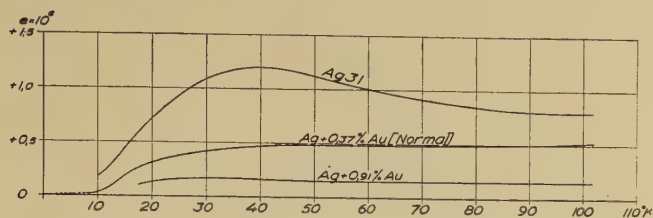


Fig. 2. Thermo-electric force in volt per degree in the absolute thermo-electric scale for Ag, Ag with 0.37 at. % Au (Normal) and Ag with 0.91 at. % Au.

§ 3. *Au with small quantities of Fe.* As we were interested to see if perhaps the high thermo-electric forces observed in the system *Cu Fe* at the liquid helium temperatures (c.f. our next paper) are due to the high degree of supersaturation of these alloys, we also investigated the analogous system *Au Fe*, where the solubility is much higher, the saturation limit being at room temperature about 20 at. % *Fe*. The

TABLE II.

Thermo-electric force in microvolt per degree for dilute alloys of Au with Fe against silveralloy-normal.							
Au + 0.065 at. % Fe		Au + 0.19 at. % Fe		Au + 1.09 at. % Fe		Au + 1.89 at. % Fe	
°K.	e	°K.	e	°K.	e	°K.	e
17.5	-13.77	17.4	-13.64	17.3	-8.37	17.5	-6.33
17.5	13.80	17.4	13.92	17.3	8.42	17.5	6.30
24.1	12.47	24.7	13.75	24.0	10.07	24.1	8.10
30.7	11.29	31.3	13.40	30.3	11.30	30.7	9.55
36.9	10.26	38.3	13.01	36.7	11.88	36.9	10.40
42.9	9.63	45.8	12.43	42.7	12.33	42.9	11.20
48.3	8.98	50.6	11.86	47.2	12.63	48.3	11.36
92.4	5.25	62.1	10.73	58.8	12.20	94.2	11.78
102.3	5.29	68.0	10.65	67.8	11.97	102.3	11.78
102.3	5.42	102.0	8.90	79.0	12.10	102.3	11.78
293.1	0.9	293.1	3.76	86.2	11.97	293.1	7.5
				94.2	12.30		
				102.6	11.81		
				275.4	7.28		



measurements were carried out down to the hydrogen temperatures for four alloys with 0.065 to 1.89 at. % Fe. The results are given in table II and are shown in the temperature diagram Fig. 3 and the concentration diagram Fig. 4.

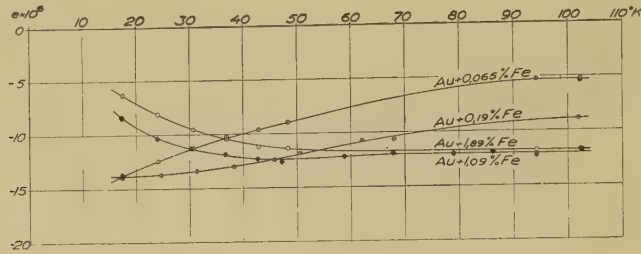


Fig. 3. Thermo-electric force in volt per degree.  
Against silver alloy-normal.

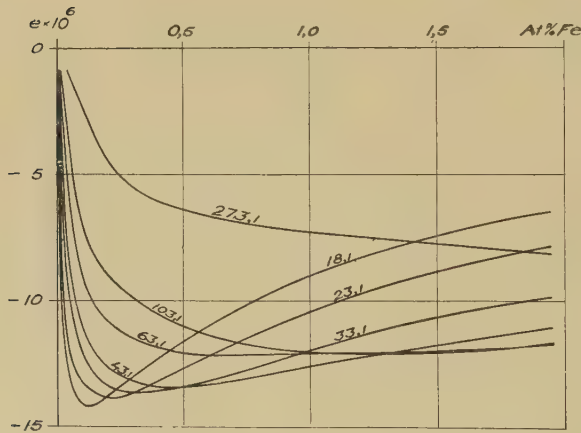


Fig. 4. Thermo-electric force in volt per degree for dilute alloys of Au with Fe as a function of the concentration of Fe. The numbers give the temperature of the isotherms on the Kelvinscale.  
Against silver alloy-normal.

In fact the curves are quite analogous to those for the system *Cu Fe* (next paper § 3) and the negative maximum value of *e* is of the same order of magnitude. There is, however, a quantitative difference between the two systems in so far as the negative maximum in the system *Au Fe* as compared with the system *Cu Fe* is displaced for a given temperature towards higher concentrations (observe the different scales in the Figures 4 of this and 3 of the next paper) and for a given concentration towards lower temperatures. This may perhaps depend upon the fact that the characteristic temperature of *Au* is smaller than that of *Cu*. Any signs of a specific difference as to the degree of supersaturation have not been found.

§ 4. *Au with small quantities of Co.* Measurements on an alloy of

Cu with 0.09 at. % Co carried out in 1929<sup>1)</sup> down to the liquid oxygen temperatures made it probable that Co as well as Fe was a suitable metal to add for getting high thermo-electric forces at low temperatures. This time we measured five alloys of Au with 0.061 to 6.71 at. % Co. The results are given in Table III and the Figs. 5 and 6. They show, that

TABLE III.

Thermo-electric force in microvolt per degree for dilute alloys of Au with Co against silveralloy-normal.									
Au + 0.061 at. % Co		Au + 0.21 at. % Co		Au + 0.95 at. % Co		Au + 2.11 at. % Co		Au + 6.71 at. % Co	
°K.	e	°K.	e	°K.	e	°K.	e	°K.	e
17.5	-11.52	17.4	-13.09	17.4	-13.93	17.5	-15.00	17.4	-11.74
17.5	11.54	26.7	17.34	23.9	17.64	17.5	15.03	26.7	15.64
24.1	12.85	36.5	20.40	30.3	21.28	24.1	18.87	36.5	19.10
30.4	13.56	42.5	21.90	36.5	24.00	30.7	22.27	42.5	20.80
36.9	13.70	48.0	22.34	42.5	26.18	36.9	24.60	48.0	22.12
42.9	13.97	57.5	23.2	48.0	27.7	42.9	27.1	58.8	23.6
48.3	13.90	60.8	23.3	56.8	28.7	48.3	28.3	60.7	23.8
94.2	13.11	66.8	23.8	62.1	29.8	94.2	37.8	67.5	25.3
102.3	12.97	93.9	25.6	68.3	30.9	102.3	38.1	87.7	28.5
102.3	12.96	275.3	19.4	102.3	35.8	102.3	37.8	275.3	39.4
293.1	7.2			275.3	37.1	293.1	47.5		

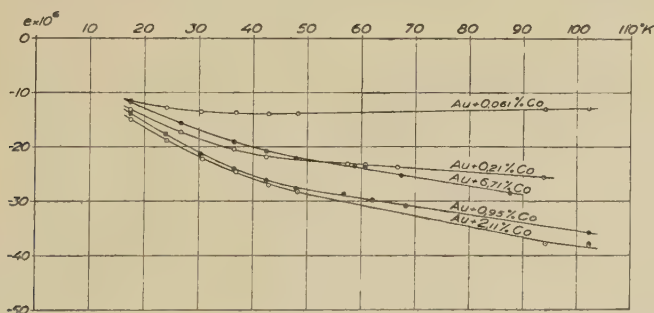


Fig. 5. Thermo-electric force in volt per degree. Against silveralloy-normal.

above about 15° K. the addition of Co to Au can give higher thermo-electric forces than the addition of Fe, whereas below this temperature the case is most probably the reverse. A detailed comparison between the systems

<sup>1)</sup> These Proceedings 33, 32, 1932. Comm. Leiden N<sup>o</sup>. 206b.

$\text{Cu Co}$  and  $\text{Au Co}$  is not yet possible, as only the one alloy of copper with 0.09 at. % Co has been measured. For the present we can only state

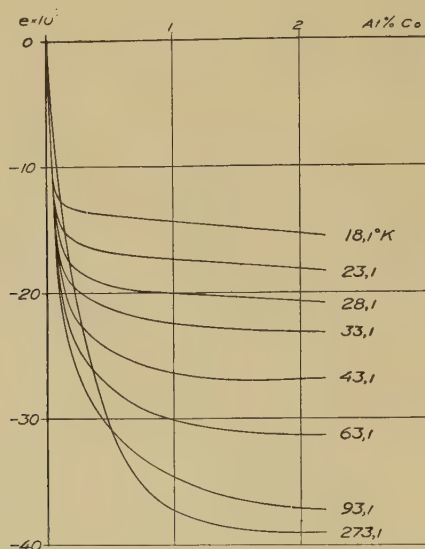


Fig. 6. Thermo-electric force in volt per degree for dilute alloys of  $\text{Au}$  with  $\text{Co}$  as a function of the concentration of  $\text{Co}$ . The numbers give the temperature of the isotherms on the Kelvinscale. Against silveralloy-normal.

that 0.1 at. %  $\text{Co}$  has a larger thermo-electric influence on  $\text{Au}$  than on  $\text{Cu}$  at about  $100^\circ\text{K}$ . A qualitative analogy of the two systems is, however, quite possible.

§ 5. *Au with small quantities of Ni.* We have measured three alloys of  $\text{Au}$  with 0.04, 0.18 and 1.16 at. %  $\text{Ni}$ . The results are given in Table IV and Fig. 7. The concentration diagram constructed in Fig. 8 is of course somewhat uncertain in the details as only three concentrations have been examined.

It seems probable, that the most dilute alloys of  $\text{Au}$  with  $\text{Ni}$  (just as those of  $\text{Au}$  or  $\text{Cu}$  with  $\text{Fe}$ ) have a negative maximum of the thermo-electric force below the liquid hydrogen temperatures. However, it is not yet quite sure to what extent the shape of the curves at the lowest temperatures are influenced by small impurities of iron.

A comparison of the present curves for the system  $\text{Au Ni}$  with those for the system  $\text{Cu Ni}$ , given in our earlier paper<sup>1)</sup>, show, that the same concentration of  $\text{Ni}$  has a larger influence on  $\text{Au}$  than on  $\text{Cu}$  (with  $\text{Co}$  the case was the same as with  $\text{Ni}$ , with  $\text{Fe}$  it was the opposite). A qualitative analogy of the two systems  $\text{Cu Ni}$  and  $\text{Au Ni}$  seems quite possible.

<sup>1)</sup> Comm. Leiden N<sup>o</sup>. 206b Fig. 2.



TABLE IV.

Thermo-electric force in microvolt per degree for dilute alloys of Au with Ni against silveralloy-normal.					
Au + 0.04 at. % Ni		Au + 0.18 at. % Ni		Au + 1.16 at. % Ni	
°K.	e	°K.	e	°K.	e
17.3	-3.02	17.3	-3.59	17.3	-4.13
17.3	3.04	17.3	3.60	17.3	4.16
23.9	2.25	23.9	3.53	24.0	4.88
30.4	1.61	30.4	3.31	30.3	5.54
36.8	1.22	36.8	3.08	42.7	6.38
42.8	0.987	42.8	2.95	47.2	6.64
48.0	0.855	48.0	2.84	58.9	6.94
59.3	0.722	59.3	2.66	67.8	7.41
68.3	0.685	68.3	2.64	79.0	8.17
77.3	0.643	77.3	2.66	86.2	8.37
85.9	0.633	85.9	2.67	94.1	9.21
94.0	0.633	94.0	2.80	102.6	9.28
102.2	0.610	102.2	2.80	275.4	14.48
273.3	0.417	273.3	3.24		

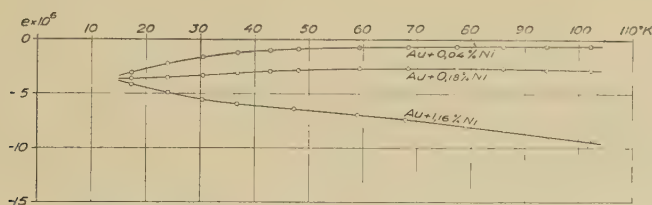


Fig. 7. Thermo-electric force in volt per degree. Against silveralloy-normal.

As far as can be made probable by extrapolations, it seems not possible to get the same high thermo-electric forces against the pure metals *Au* or *Cu* at low temperatures by adding *Ni* as by adding *Fe* or *Co*.

§ 6. *Au with small quantities of Mn, Cr and Ti.* We have also measured some dilute alloys of *Au* with *Mn*, *Cr* and *Ti*, the neighbours of *Fe*, *Co* and *Ni* in the transition group of the fourth period of the periodic system. The results are given in Table V and Fig. 9. These alloys

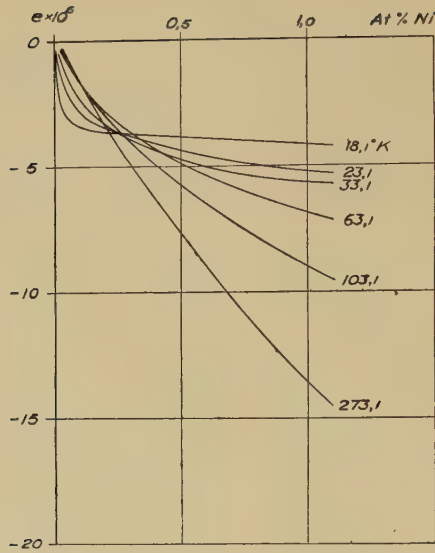


Fig. 8. Thermo-electric force in volt per degree for dilute alloys of *Au* with *Ni* as a function of the concentration of *Ni*. The numbers give the temperature of the isotherms on the Kelvinscale. Against silveralloy-normal.

TABLE V.

Thermo-electric force in microvolt per degree against silveralloy-normal.					
Au + 0.2 at. % Ti		Au + 3.65 at. % Cr		Au + 2.08 at. % Mn	
°K.	e	°K.	e	°K.	e
17.4	-0.855	17.4	-0.508	17.3	-1.23 <sub>5</sub>
24.7	0.883	17.4	0.503	17.3	1.25
31.3	0.807	24.7	0.917	23.9	1.59
38.3	0.756	31.3	1.243	30.4	1.76 <sub>5</sub>
45.8	0.633	38.3	1.594	36.8	1.86 <sub>5</sub>
50.6	0.562	45.8	1.916	42.8	1.88
62.1	0.361	50.6	2.10	48.0	1.85 <sub>5</sub>
68.0	0.251	62.1	2.48	59.3	1.71
102.0	+0.236	68.0	2.75	68.3	1.65
295.0	1.97	102.0	3.77	77.3	1.54
		295.0	8.42	85.9	1.48
				94.0	1.45
				102.2	1.24
				275.3	0.09

TABLE VI.

Thermo-electric force in microvolt per degree against silver-alloy-normal.																
°K.	°C.	Au — Fe				Au — Co					Au — Ni			Au — Ti	Au — Cr	Au — Mn
		at. % Fe		at. % Fe	1.89	at. % Co		at. % Co	0.95	2.11	6.71	at. % Ni		at. % Ni	0.18	1.16
		0.065	0.19	1.09	1.89	0.061	0.21	0.95	2.11	6.71	0.04	0.18	1.16	0.2	3.65	2.08
18.1	—255	—13.66	—13.85	—8.65	—6.54	—11.65	—13.4	—14.3	—15.35	—12.1	—2.95	—3.60	—4.24	—0.86	—0.60	—1.30
23.1	250	12.64	13.74	10.08	7.94	12.65	15.8	17.3	18.25	14.2	2.44	3.52	4.82	0.86	0.83	1.55
28.1	245	11.71	13.48	11.06	9.05	13.3	17.9	20.05	20.8	16.2	1.82	3.39	5.33	0.85	1.10	1.73
33.1	240	10.88	13.32	11.66	9.94	13.7	19.6	22.5	23.2	18.0	1.43	3.23	5.73	0.82	1.33	1.83
38.1	235	10.18	13.00	12.07	10.62	13.9	20.9	24.6	25.25	19.55	1.16	3.06	6.00	0.76	1.56	1.87
43.1	230	9.57	12.61	12.37	11.10	13.95	21.85	26.3	26.95	20.85	0.99	2.93	6.23	0.68	1.78	1.87
53.1	220	8.4	11.70	12.30	11.58	13.85	22.8	28.45	29.4	22.8	0.77	2.75	6.69	0.52	2.18	1.80
63.1	210	7.3	10.77	12.10	11.70	13.7	23.5	30.0	31.3	24.5	0.70	2.70	7.15	0.34	2.55	1.70
73.1	200	6.4	10.05	12.05	11.75	13.5	24.2	31.5	33.3	26.1	0.66	2.66	7.70	0.17	2.89	1.60
83.1	190	5.7	9.45	12.05	11.76	13.3	24.9	32.9	35.3	27.7	0.64	2.57	8.29	± 0	3.20	1.50
93.1	180	5.4	9.10	12.05	11.78	13.15	25.55	34.4	37.2	—	0.61	2.74	8.90	+0.13	3.51	1.40
103.1	170	5.3	8.87	12.05	11.76	12.95	—	35.9	38.6	—	0.60	2.83	9.50	0.25	3.80	1.29
273.1	± 0	—	—	7.4	—	—	19.5	37.1	—	39.4	0.42	3.24	14.4	—	—	0.09
293.1	+ 20	0.9	3.8	—	7.5	7.2	—	—	47.5	—	—	—	—	1.96	8.4	—



give no such high thermo-electric forces against *Au* as the alloys of *Au* with *Fe* and *Co*. It should be noticed that the alloy of *Au* with *Ti* at high

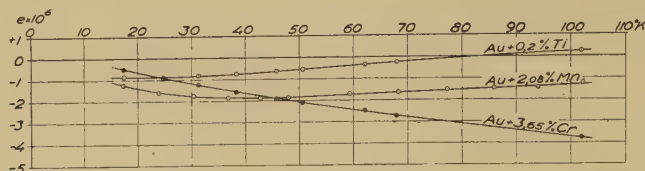


Fig. 9. Thermo-electric force in volt per degree. Against silver-alloy-normal.

temperatures is positive and at low temperatures negative against the pure metal (analogous to the dilute alloys of *Pt* with *Rh*, investigated in 1929)<sup>1)</sup>.

§ 7. *Thermo-electric forces per degree at corresponding temperatures.* Table VI gives graphically interpolated values of the thermo-electric forces against the normal of the gold alloys dealt with in this paper. The temperatures are the same as given in the corresponding tables of our earlier papers. The thermo-electric force per degree on the absolute thermo-electric scale introduced in Suppl. N<sup>o</sup>. 69b is to be obtained by adding the values of Table III of that paper.

### Summary.

Thermo-electric forces against a silver-alloy normal were measured down to the temperatures obtainable with liquid or solid hydrogen for *Ag* and an alloy of *Ag* with *Au* and for *Au* with small quantities of *Fe*, *Co*, *Ni*, *Mn*, *Cr* or *Ti* respectively.

<sup>1)</sup> Comm. Leiden N<sup>o</sup>. 206b Fig. 2.

**Physics.** — *Measurements on Thermo-Electric Forces down to Temperatures Obtainable with Liquid Helium.* By G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. (Communication N<sup>o</sup>. 217e from the Physical Laboratory at Leiden.)

(Communicated at the meeting of January 30, 1932.)

§ 1. *Introduction.* This paper deals with the measurements on thermo-electric forces referred to in Comm. N<sup>o</sup>. 217d, of platinum and of some binary alloys of *Cu* with small quantities of *Fe*, which were investigated down to the temperatures obtainable with liquid helium. For the method followed and the apparatus used we refer to §§ 1 and 2 of the paper mentioned.

§ 2. *Results for Pt and an alloy of Pt with Au.* It seems to be rather difficult to get an accurate knowledge of the thermo-electric properties of real pure, not supraconducting metals at the lowest temperatures, as small impurities seem to have a great influence here. Measurements of commercial pure metals will probably only give an approximate orientation. We have tried to get such an orientation by measurements on physically pure *Pt* from HERAEUS in Hanau and on pure *Cu* obtained for spectroscopic purposes from HILGER in London.

The copper contained, however, according to the report of a spectroscopical analysis got from the firm, 0.004 at. % *Fe*, and this impurity was, as will be seen in the next paragraph, sufficient to give thermo-electric properties quite different from those of pure copper.

The platinum gave the values collected in table I and the curve marked  $Pt_{31}$  in Fig. 1. The curve crosses the axis at 12° K. and seems to approach the absolute zero point from the negative side of the axis. However, we are not allowed to assume that this should be characteristic of the pure *Pt*. Our earlier measurements on dilute alloys of *Pt* with *Rh*<sup>1)</sup>, as well as new measurements on *Pt* with 4.0 at. % *Au* down to the temperature of liquid hydrogen and in fact all our experiences hitherto from the lowest temperatures show, that dilute alloys are thermo-electrically negative against the corresponding pure metal. Thus it is quite possible that the negative values (negative also in the absolute thermo-electric scale) arise from impurities. In fact another sample of physically pure *Pt* from HERAEUS measured in 1929<sup>2)</sup> and given again in Fig. 1 as  $Pt_{29}$  lies more to the positive side.

1) Comm. N<sup>o</sup>. 206b. These Proceedings **33**, 32, 1930.

2) Comm. N<sup>o</sup>. 206a. These Proceedings **33**, 17, 1930.

TABLE I.

Thermo-electric force in microvolt per degree for pure and alloyed Pt against silveralloy-normal.					
Pt <sub>31</sub> (Heraeus)				Pt + 4 at. % Au	
°K.	e	°K.	e	°K.	e
4.15	-0.6	24.0	+2.07	17.4	0.00
5.17	0.81	30.3	3.07	17.4	-0.02
5.42	0.78	36.7	3.88	24.7	+0.54
7.72	0.55	42.7	4.38	31.3	1.06
7.78	0.59	47.2	4.88	38.3	1.58
10.4	0.23	58.9	4.97	45.8	1.98
10.6	0.16	67.9	4.95	50.6	2.06
10.8	0.17	79.0	4.73	62.1	2.15
11.3	0.04	86.2	4.26	68.0	2.14
12.5	+0.07	94.2	4.00	102.0	1.06
13.3	0.27	102.7	3.57	295.0	-7.95
17.3	0.92	275.4	-5.18		

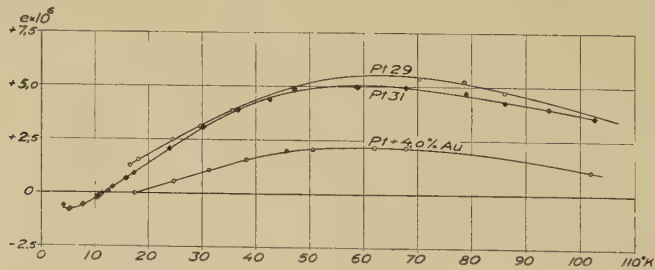


Fig. 1. Thermo-electric force in volt per degree. Against silveralloy normal.

§ 3. *Cu with small quantities of Fe.* The interesting high thermo-electric forces, obtained from our earlier measurements for an alloy of Cu with only 0.075 at. % Fe at the temperature of liquid hydrogen (Comm. N<sup>o</sup>. 206b), have led to a comprehensive investigation of the thermo-electric forces of copper with small quantities of Fe as a function of temperature and concentration and to the use of those dilute alloys for an examination of the way in which the thermo-electric force decreases as the absolute temperature approaches to zero. Besides the wire with 0.075 at. % Fe, for which we have got results in good agreement with



our earlier measurements, we have measured alloys of *Cu* with 0.004, 0.03, 0.10, 0.30 and 0.87 at. % *Fe*, the four first of them down to the temperature of liquid helium. The alloys were made from a copper from HILGER (containing 0.004 at. % *Fe*) by melting with *Fe* in vacuum. They were carefully homogenised and the homogeneity was controlled by measurements of the electrical resistance in different parts of the sample. The concentrations were obtained by weighing and by the measurements of the electrical resistance. The results of the thermo-electric measurements have been collected in table II and are shown graphically in Fig. 2. In this Figure we also give again the results of earlier measurements (Comm. N<sup>o</sup>. 206a) on technically pure *Cu*.

TABLE II.

Thermo-electric force in microvolt per degree for dilute alloys of <i>Cu</i> with <i>Fe</i> against silveralloy-normal.							
<i>Cu</i> + 0.004 at. % <i>Fe</i>				<i>Cu</i> + 0.03 at. % <i>Fe</i>			
°K.	<i>e</i>	°K.	<i>e</i>	°K.	<i>e</i>	°K.	<i>e</i>
1.63	1.97	22.6	8.06	1.63	3.76	22.6	14.92
1.73	2.15	24.0	7.98	1.73	4.20	24.0	14.96
1.73	2.17	24.0	8.04	1.73	4.28	24.0	15.05
3.00	3.98	27.2	7.12	3.00	6.95	27.2	14.35
3.84	4.82	30.4	6.44	3.84	8.13	30.4	13.68
5.22	6.34	30.5	6.41	5.22	10.35	30.5	13.74
5.73	6.66	31.5	6.12	5.73	10.71	31.5	13.66
5.88	6.85	36.1	4.95	5.88	10.97	36.1	12.52
6.57	7.06	36.7	4.90	6.57	11.57	36.7	12.40
7.25	7.62	36.9	4.85	7.25	12.04	36.9	12.35
8.20	8.06	42.5	3.65	8.20	13.53	42.5	11.22
9.17	8.61	42.6	3.67	9.17	13.38	42.6	11.27
9.72	8.91	43.3	3.44	9.72	13.65	43.3	10.97
9.96	9.52	48.0	2.61	9.96	14.05	48.0	9.80
11.8	9.23	48.0	2.62	11.8	14.84	48.0	9.87
16.8	8.92	65.9	0.81	16.8	15.02	65.9	6.58
17.3	9.12	84.1	0.30	17.3	15.20	84.1	5.10
17.3	9.16	93.8	0.18	17.3	15.25	93.8	4.56
21.0	8.62			21.0	15.32	275.6	1.62

TABLE II (Continued).

Cu + 0.075 at. % Fe		Cu + 0.10 at. % Fe		Cu + 0.30 at. % Fe		Cu + 0.87 at. % Fe	
°K.	e	°K.	e	°K.	e	°K.	e
17.0	-15.72	2.50	-6.34	2.50	-3.92	17.3	9.78
22.2	15.94	2.62	6.56	2.62	4.18	17.3	9.83
22.7	15.92	3.45	7.88	3.45	5.23	17.4	9.83
26.1	15.60	3.50	7.92	3.50	5.31	17.4	9.83
26.6	15.95	5.30	10.27	5.30	6.95	17.4	9.93
31.2	15.46	7.30	12.09	7.30	8.41	23.9	10.98
34.9	15.00	11.1	14.82	11.1	12.07	23.9	11.10
35.3	14.82	13.3	15.27	13.3	13.10	30.3	11.79
42.5	13.78	17.0	15.75	17.0	13.27	30.4	11.76
52.0	12.18	22.2	16.08	22.2	13.96	36.5	12.15
64.0	10.70	22.7	16.50	22.7	14.40	36.8	12.14
70.5	10.15	26.1	15.76	26.1	14.14	42.5	12.44
85.1	8.72	26.6	15.75	26.6	14.38	42.8	12.37
95.3	7.98	31.2	15.76	31.2	14.53	48.0	12.37
275.8	3.92	34.9	15.32	34.9	14.40	48.0	12.44
		35.3	15.32	35.3	14.54	59.3	12.03
		42.6	14.32	42.5	14.36	62.1	11.98
		52.0	12.97	52.0	14.58	68.0	12.05
		64.0	11.74	64.0	14.37	68.3	11.97
		70.5	10.84	70.5	13.38	77.3	11.98
		85.1	9.74	85.1	12.42	85.9	11.95
		95.3	8.96	95.3	11.80	94.0	12.34
		275.8	4.66	275.8	8.47	102.0	12.04
						102.2	11.95
						275.6	10.55

The results seem to state rather clearly that the thermo-electric force per degree ( $e$ ) is in the neighbourhood of the absolute zeropoint proportional to the absolute temperature ( $T$ ). With increasing temperature  $e$  first reaches a (negative) maximum and then decreases. With increasing

concentration ( $c$ ) the maximum is displaced toward higher temperatures.

From the measurements we have also calculated diagrams giving  $e$  as

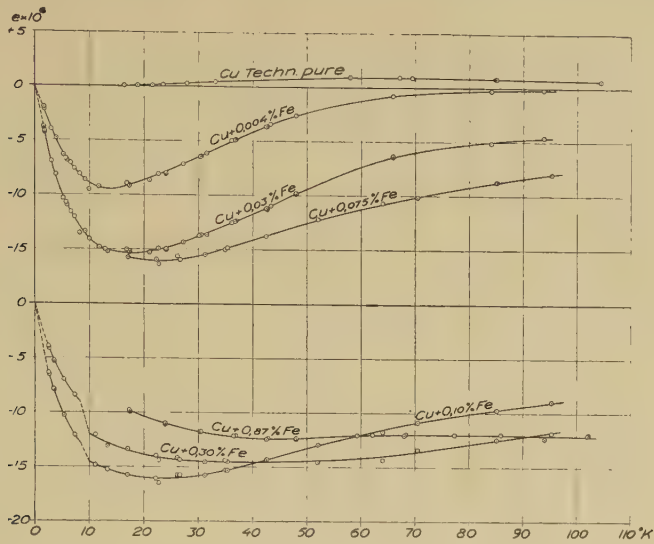


Fig. 2. Thermo-electric force in volt per degree. Against silver-alloy normal

a function of  $c$  for different constant temperatures. Such isotherms have been put together in Fig. 3. The curves show a striking likeness to the curves in Fig. 2. An analysis of  $e$  as a function of  $T$  and  $c$  looks very interesting and will probably be carried out later on.

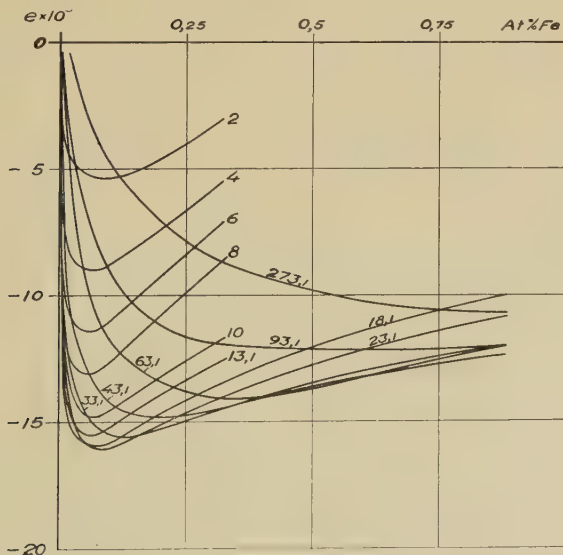


Fig. 3. Thermo-electric force in volt per degree for dilute alloys of Cu with Fe as a function of the concentration of Fe. The numbers give the temperature of the isotherms in the Kelvin-scale. Against silver-alloy-normal.



The alloys with 0.1 and 0.3 at. % *Fe* show, between 8 and 10° K., a discontinuity as well in thermo-electromotive force (see Fig. 4) as in the thermo-electric force per degree (see Fig. 2). Possibly the fact that in Fig. 2 for *Cu* with 0.03 and 0.004 at. % *Fe* the points for the temperature range mentioned lie a little beside the curves, is also a sign of traces of such a discontinuity. The discontinuity in the alloys with 0.1 and 0.3 at. % *Fe* was studied by repeated variations of the temperature up and down and was proved to be reversible. For the present the nature of the discontinuity is, however, quite unknown.

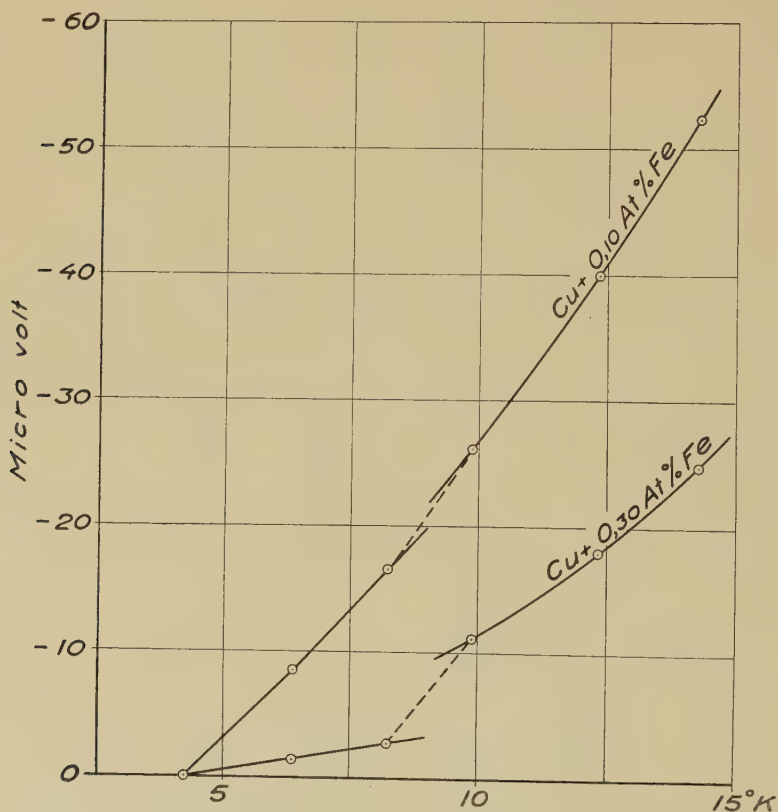


Fig. 4. E. m. f. against *Cu* with 0.004 at. % *Fe*. Cold junction at 4.24° K.

It may be mentioned, that the alloys of *Cu* with *Fe* are highly supersaturated at room temperature and are obtained as homogeneous solid solutions, at the highest concentrations here used, only by rapid cooling from about 800° C. According to TAMMANN and OELSEN<sup>1)</sup> the solubility of *Fe* in *Cu* should be only 10–11 at. % *Fe* in the equilibrium state at room temperature (extrapolated value). The supersaturated state is, however,

<sup>1)</sup> G. TAMMANN and W. OELSEN, Z. f. allg. u. anorg. Chem. **186**, 257, 1930.

known as practically stable at all temperatures for concentrations below about 0.1 at. % Fe.

§ 4. *Thermo-electric forces per degree at corresponding temperatures.* The tables III and IV give graphically interpolated values of the thermo-electric forces against the normal of the wires dealt with in this paper.

In Table III we added corresponding values for lead and tin and for pure and alloyed silver derived from the results obtained in Comm. N<sup>o</sup>. 217c and N<sup>o</sup>. 217d.

Above  $-255^{\circ}\text{C}$ . the temperatures are the same as those given in the corresponding tables of our earlier papers. The thermo-electric force per degree on the absolute thermo-electric scale is obtained by adding the values of table III of Suppl. N<sup>o</sup>. 69b.

TABLE III.

Thermo-electric force in microvolt per degree against silveralloy-normal.							
°K.	°C.	Pb	Sn	Ag <sub>31</sub>	Ag + 0.91 at. % Au	Pt <sub>31</sub>	Pt + 4.0 at. % Au
2.0	-271.1	0.00	0.00				
4.0	269.1	0.00	-0.01			-0.73	
6.0	267.1	-0.01	0.05			0.74	
8.0	265.1	0.13	0.11			0.55	
10.0	263.1	0.43	0.19	+0.15		0.27	
13.1	260	0.82	0.39	0.21		+0.23	
18.1	255	1.01	0.75	0.35	-0.16	1.05	+0.03
23.1	250	1.10	1.01	0.49	0.20	1.92	0.42
28.1	245	1.14	1.22	0.63	0.23	2.73	0.82
33.1	240	1.17	1.40	0.71	0.27	3.45	1.20
38.1	235	1.19	1.53	0.73	0.30	4.03	1.55
43.1	230	1.21	1.66	0.71	0.32	4.50	1.85
53.1	220	1.22	1.77	0.60	0.33	4.98	2.12
63.1	210	1.23	1.83	0.49	0.33	5.03	2.15
73.1	200	1.24	1.88	0.41	0.33	4.80	2.05
83.1	190	1.26	1.94	0.34	0.34	4.44	1.81
93.1	180	1.32	1.99	0.29	0.34	4.03	1.45
103.1	170		2.03	0.28	0.35	3.57	1.01
275.6	+ 2.5		2.43	0.21	0.38	-5.18	

TABLE IV.

Thermo-electric force in microvolt per degree against silveralloy-normal.							
°K.	°C.	Cu + 0.004 at. % Fe	Cu + 0.03 at. % Fe	Cu + 0.075 at. % Fe	Cu + 0.10 at. % Fe	Cu + 0.30 at. % Fe	Cu + 0.87 at. % Fe
2.0	—271.1	—2.6	—4.85		—5.35	—3.35	
4.0	269.1	5.05	8.65		8.75	5.85	
6.0	267.1	6.9	11.1		11.0	7.55	
8.0	265.1	8.05	12.8		12.6	9.0	
10.0	263.1	8.95	14.1		14.55	12.0	
13.1	260	9.55	15.0		15.2	12.8	
18.1	255	8.95	15.4	—15.85	15.85	13.65	—10.05
23.1	250	8.0	14.95	16.05	16.1	14.2	10.9
28.1	245	6.9	14.15	15.8	15.95	14.4	11.6
33.1	240	5.75	13.15	15.2	15.5	14.6	12.05
38.1	235	4.6	12.1	14.4	14.95	14.55	12.3
43.1	230	3.5	11.05	13.6	14.25	14.55	12.4
53.1	220	1.9	8.7	12.1	12.85	14.4	12.25
63.1	210	1.0	6.75	10.9	11.7	14.05	12.05
73.1	200	0.5	5.7	9.8	10.65	13.4	12.0
83.1	190	0.3	5.05	8.9	9.85	12.65	12.0
93.1	180	0.2	4.7	8.1	9.15	11.9	12.05
103.1	170						12.15
273.1	±0		1.66	3.98	4.72	8.52	10.57

§ 5. *Thermo-couples for temperature measurements at low temperatures.* From this and the preceding paper (Comm. N<sup>o</sup>. 217d) one may conclude that the dilute alloys of *Au* with *Co* or *Fe* and of *Cu* with *Fe* may be used as sensible thermo-couples for temperature measurements at low temperatures. The gold-alloys are to be preferred as they are not supersaturated at room temperature and hence are obtained in the homogeneous state without rapid cooling. As a promising couple we may propose a combination of a dilute alloy of *Au* with *Co*, say one with about 1 at. % *Co*, and a dilute *Ag Au*-alloy with about 1 at. % *Au*. As will be seen from Figs. 1, 5 and 6 and Tables I and III of Comm. N<sup>o</sup>. 217d this couple will have high values of the thermo-electric force per degree (*e*) for all temperatures from the ice-



point down to the lowest temperature of liquid hydrogen. So it will give in microvolt per degree: at  $\pm 0^\circ$  C. about 37, at  $-180^\circ$  C. about 34, at  $-220^\circ$  C. about 28, at  $-250^\circ$  C. about 17, and at  $-255^\circ$  C. about 14. Also at the temperature of liquid helium high values of  $e$  may be expected if they diminish with the temperature in the same way in the system *Au-Co* as in the system *Cu-Fe*. As to the proposed silver-alloy it appears from the diagram of the absolute thermo-electric force (Fig. 2 of Comm. N<sup>o</sup>. 217d), that it may be expected to give rather small thermo-electric variations of its own and thus lead to a smooth  $e$ ,  $T$ -curve. *Ag* is to be preferred to *Cu* or *Au* as it is easier to get it free from traces of *Fe*, and alloyed *Ag* is to be preferred to the pure metal also for the reason that the thermal conductivity does not increase to unsuitable high values at the lowest temperatures. Of course special measurements are necessary to find the most suitable concentrations and to confirm the expectations as to the usefulness of the thermo-couple also in the liquid helium temperatures.

We are glad to record our thanks to the NOBEL-committee for physics, who supported our researches by a subvention.

#### *Summary.*

Thermo-electric forces against a silveralloy-normal were measured down to the temperatures which are obtainable with liquid helium, for *Pt* and for alloys of *Cu* with small quantities of *Fe*.

For the last-mentioned alloys the thermo-electric force per degree near absolute zero is proportional to  $T$ . At increasing temperatures  $e$  reaches a maximum, after which  $e$  decreases. With increasing concentration of *Fe* this maximum is displaced towards higher temperatures.

As a sensitive thermo-element for the temperature range of liquid hydrogen and liquid helium the authors recommend the combination *Au* with about 1 at. % *Co* against *Ag* with about 1 at. % *Au*.

**Astronomy.** — *Mittlere Lichtkurven von langperiodischen Veränderlichen.*

VI. *R Cygni*. Von A. A. NIJLAND.

(Communicated at the meeting of January 30, 1932.)

Instrumente: *S* und *R*. Die Beobachtungen wurden alle auf *R* reduziert: die Reduktion  $R-S$  beträgt  $-0^m.34$ . Spektrum *Se* (*Harv. Ann.* 79 S. 187).

Gesamtzahl der hier zu besprechenden Beobachtungen 729 (2416826 bis 2426648).

Karte: HAGEN, *Atlas Stell. var. Series III*.

Der Stern *B* kommt mit den Helligkeiten  $6^m.48$ ,  $6^m.39$  in *Harv. Ann.* 74 vor. Die Stufenskala bezieht sich auf die Grösse  $10^m.0$ ; der Stufenwert

TABELLE I. Vergleichsterne.

	BD	HAGEN	St.	HA 29	HA 37	HA 98	PD	PD red.	H
C	+ 48.2914	—	72.8	—	<sup>m</sup> 6.19	<sup>m</sup> 6.19 Mb	<sup>m</sup> 6.14 WG+	<sup>m</sup> 6.09	<sup>m</sup> 6.14
B	49.3059	2	67.8	<sup>m</sup> 6.76	—	6.63 G5	6.68 WG	6.59	6.65
A	48.2918	—	63.0	—	7.17	7.26 K2	7.13 G	7.18	7.14
a	49.3033	—	58.0	7.57	—	7.62 K0	—	—	7.66
b	50.2844	3	54.4	7.92	—	7.90 G5	—	—	8.03
c	49.3051	5	47.5	9.01	—	—	—	—	8.73
d	49.3061	10	44.1 <sup>5</sup>	—	—	—	—	—	9.07
e	49.3065	14	39.6	9.48	—	—	—	—	9.53
f	—	25	37.4	—	—	—	—	—	9.76
g	49.3068	31	32.6	10.22	(10.90)	—	—	—	10.25
h	—	33	29.2	—	—	—	—	—	10.60
j	—	36	26.9	—	—	—	—	—	10.84
k	—	38	21.4	—	—	—	—	—	11.40
l	—	44	20.1	—	—	—	—	—	11.53
m	—	50	17.3	—	—	—	—	—	11.82
x	—	43	17.5	—	11.86	—	—	—	(11.80)
n	—	56	14.6 <sup>5</sup>	12.04	12.29	—	—	—	12.10
p	—	59	11.0	12.19	12.09	—	—	—	12.47
q	—	64	6.6	(12.16)	12.72	—	—	—	12.92
r	—	73	0.0	—	—	—	—	—	13.59

ist 0<sup>m</sup>.102. Die Sterne *h* bis *l* wurden viermal an die Sichtbarkeitsgrenze von *S* angeschlossen; für *k* folgt daraus der allerdings nicht sehr genaue Wert 11<sup>m</sup>.60. Der Veränderliche sinkt im Minimum meistens etwa 0<sup>m</sup>.2—0<sup>m</sup>.4 unter die Helligkeit des Sterns *r* und also bis nahe an die Grenze des Zehnzöllers hinab, und ist dann wegen der Nähe von  $\theta$  Cygni (4<sup>m</sup>.5) ein sehr schwieriges Objekt. Aus 18 Anschlüssen an diese Grenze folgt für *r* die Grösse 13<sup>m</sup>.74. Die Grössen 10<sup>m</sup>.90 für *g* aus *Harv. Ann.* 37 und 12<sup>m</sup>.16 für *q* aus *Harv. Ann.* 29 mussten unberücksichtigt bleiben. Übrigens ist der Anschluss der Stufenskala an die photometrischen Helligkeiten nicht unbefriedigend.

Es liegen 101 Schätzungen der Farbe vor, welche aber für vier Fünftel aus den Jahren 1905—1911 stammen. Aus der Tabelle IIa geht hervor, dass die Farbe sich im Laufe der Jahre 1905 bis 1931 kaum geändert hat.



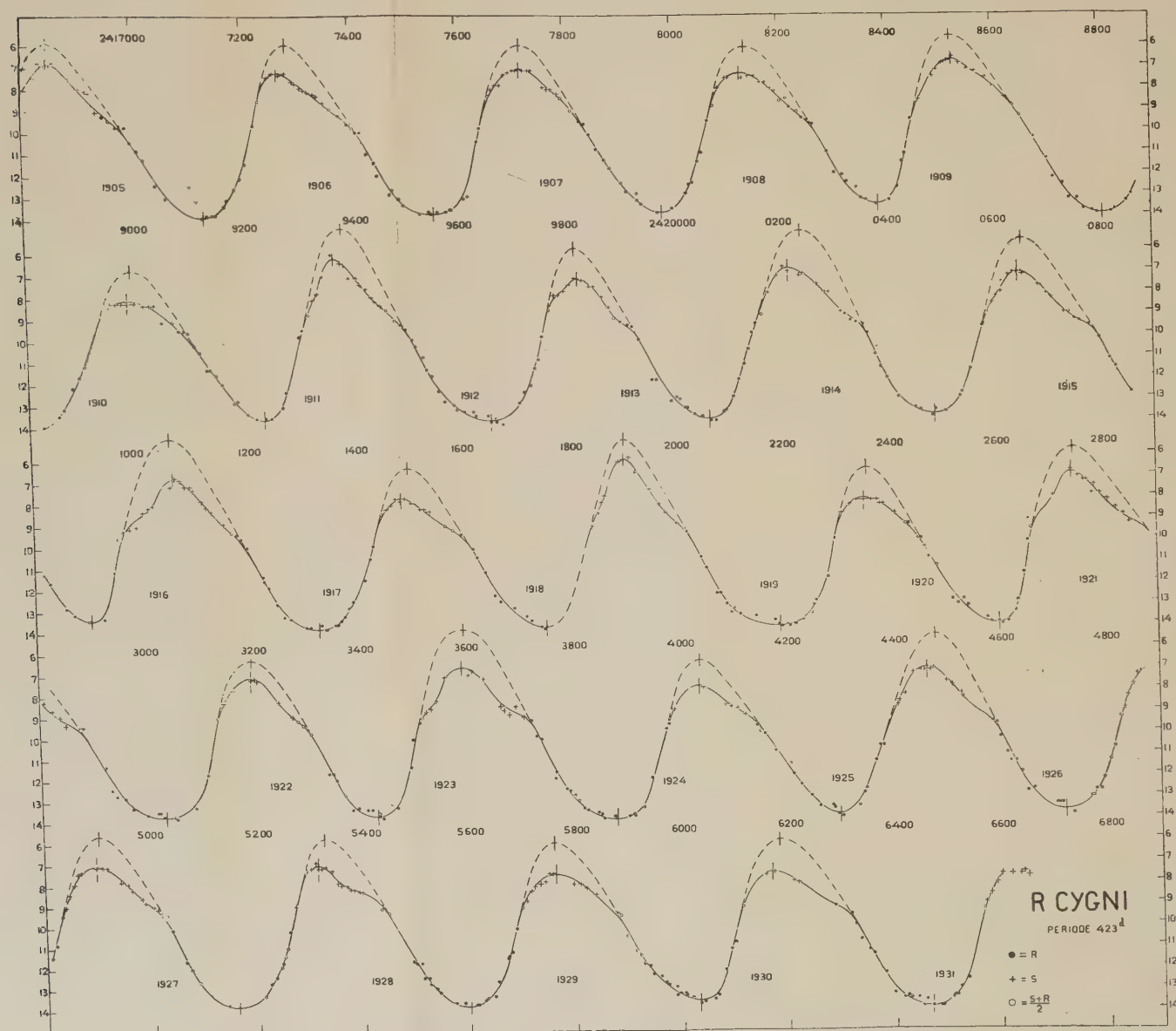


Fig. 1



Wie bei *R Trianguli* ist aber eine Abhängigkeit von der Helligkeit deutlich ausgeprägt: aus der Tabelle IIb ist ersichtlich, dass der Stern in meiner Auffassung bei 7<sup>m</sup>.6 die geringste Färbung (4<sup>c</sup>.00) gezeigt hat. Das allgemeine Mittel ist 4<sup>c</sup>.49.

TABELLEN IIa und IIb. Farbenschätzung.

Zeitraum	<i>m</i>	Farbe	Grösse	<i>m</i>	Farbe
<sup>241</sup> 6948—7366	18	<sup>c</sup> 4.44	<sup>m</sup> 6.76	13	<sup>c</sup> 4.50
7382—7788	18	4.08	7.11	12	4.29
7795—8255	18	4.58	7.30	13	4.02
8265—9066	18	4.47	7.67	12	4.00
<sup>242</sup> 9301—0760	18	4.75	8.07	13	4.12
1063—5321	11	4.73	8.45	12	4.33
	101	4.51	9.17	13	5.04
			9.87	13	5.65
				101	4.49

Die Figur 1 enthält die Beobachtungen, alle auf *R* reduziert. Die Reihe der Abweichungen (Beobachtung minus Kurve) zeigt 268 Plus-, 256 Minuszeichen, 205 Nullwerte, 266 Zeichenfolgen, 257 Zeichenwechsel. Ein Einfluss des Mondscheines auf die Helligkeitsschätzung ist nicht bemerkbar. Es verteilen sich auf 213 bei Mondschein angestellte Beobachtungen die Abweichungen wie folgt: 78 Plus-, 72 Minuszeichen, 63 Nullwerte.

Die Tabelle III enthält die aus der Kurve abgelesenen Epochen der Minima *m* und der Maxima *M*, nebst der Vergleichung mit den einfachen Elementen:

$$\begin{aligned} &2421769^d + 423^d E \text{ (für die Minima)} \\ \text{und} &2421922 + 423 E \text{ (für die Maxima).} \end{aligned}$$

Aus den Spalten *B—R* geht hervor, dass die Periode von *R Cygni* für den hier betrachteten Zeitraum in Zunahme begriffen ist. Aus einer graphischen Lösung folgen die Elemente *F*:

$$\begin{aligned} &2421753^d + 423^d E + 0^d.42 E^2 \text{ (für die Minima)} \\ \text{und} &2421906 + 423 E + 0.42 E^2 \text{ (für die Maxima).} \end{aligned}$$

Obgleich die Berücksichtigung des quadratischen Gliedes die Quadratsummen der Abweichungen, für die Minima und die Maxima zusammen, von 13869 auf 8243 herabdrückt, halte ich die hier angedeutete säkuläre Veränderung der Periode nicht für reell, und ich würde jedenfalls ein

TABELLE III.

E	Minima m					Maxima M				
	B	$\nu$	R	B-R	B-F	B	$\nu$	R	B-R	B-F
-12	—	—	—	—	—	<sup>241</sup> 6847	<sup>m</sup> 6.8	6846	+ 1	-43
-11	<sup>241</sup> 7129	<sup>m</sup> 13.9	7116	+13	-22	7268	7.2	7269	- 1	-36
-10	7558	13.8	7539	+19	- 7	7719	7.1	7692	+27	+ 1
- 9	7981	13.8	7962	+19	+ 1	8129	7.3	8115	+14	- 4
- 8	8385	13.4	8385	0	-11	8527	6.8	8538	-11	-22
- 7	8809	14.0	8808	+ 1	- 4	8984	8.1	8961	+23	+18
- 6	9235	13.7	9231	+ 4	+ 5	9366	6.2	9384	-18	-17
- 5	9657	13.8	9654	+ 3	+ 9	9819	7.3	9807	+12	+18
- 4	<sup>242</sup> 0064	13.8	0077	-13	- 4	<sup>242</sup> 0213	6.8	0230	-17	- 8
- 3	0485	13.7	0500	-15	- 3	0644	7.1	0653	- 9	+ 3
- 2	0904	13.4	0923	-19	- 5	1058	6.8	1076	-18	- 4
- 1	1328	13.9	1346	-18	- 2	1485	7.7	1499	-14	+ 2
0	1753	13.9	1769	-16	0	1899	6.1	1922	-23	- 7
+ 1	2189	14.0	2192	- 3	+13	2347	8.0	2345	+ 2	+18
+ 2	2600	14.0	2615	-15	- 1	2739	6.9	2768	-29	-15
+ 3	3030	13.8	3038	- 8	+ 4	3196	7.1	3191	+ 5	+17
+ 4	3430	13.7	3461	-31	-22	3592	6.8	3614	-22	-13
+ 5	3879	14.0	3884	- 5	+ 1	4033	7.7	4037	- 4	+ 2
+ 6	4296	13.8	4307	-11	-10	4461	6.9	4460	+ 1	+ 2
+ 7	4719	13.7	4730	-11	-16	4897	7.0	4883	+14	+ 9
+ 8	5159	13.8	5153	+ 6	- 5	5315	7.0	5306	+ 9	- 2
+ 9	5600	13.9	5576	+24	+ 6	5763	7.5	5729	+34	+16
+10	6030	13.6	5999	+31	+ 5	6167	7.5	6152	+15	-11
+11	6467	14.0	6422	+45	+10	—	—	—	—	—
		13.80			$\pm 7$		7.12			$\pm 12$

periodisches Glied vorziehen. PRAGER's Katalog für 1932 gibt den Periodenwert  $428^{\text{d}}.4$  und das aus sämtlichen von mir seit d. J. 1905 in den *Astr. Nachr.* mitgeteilten Epochen der Minima und Maxima abgeleitete allgemeine Mittel ist  $423^{\text{d}}.8$ . Meine Beobachtungen deuten jedenfalls auf

eine viel stärkere Variabilität der Periode als wie es nach den für den Zeitraum 1852—1915 geltenden Angaben der *G. und L.* II S. 210 zu erwarten wäre. Auch bei diesem Stern genügen offenbar die sich nunmehr über 80 Jahre erstreckenden Beobachtungen keineswegs, um das wahre Gesetz des Lichtwechsels an den Tag treten zu lassen.

Die extremen Werte des Lichtwechsels sind:

$$\left. \begin{array}{l} \text{Minimum: } v = 13^{\text{m}}.80 \pm 0^{\text{m}}.32 \\ \text{Maximum: } v = 7.12 \pm 0.98 \end{array} \right\} \text{ (m.F.)}$$

Die Amplitude beträgt somit  $6^{\text{m}}.68$ .

Es wurde wieder der mittlere Verlauf der Lichtkurve in der Nähe der beiden Hauptphasen durch Ablesung der Helligkeit für je  $10^{\text{d}}$  abgeleitet. Die beiden Teilkurven schliessen sich vorzüglich an einander an (s. die Fig. 2) und geben zusammen den Verlauf der mittleren Kurve *B* (Tabelle IV).

Wie bei *S Ursae Majoris*, bekommt man auch bei *R Cygni* den starken Eindruck, dass der natürliche Verlauf der Aufhellung oft durch einen hemmenden Prozess gestört wird, der das Maximum niedriger erscheinen lässt, als erwartet werden konnte.

Die Störung macht sich besonders im Anfang des Abstiegs bemerkbar (s. die Maxima 2416847, 7268, 9366, 9819, 2420213, 0644, 1485, 3592 und 5315), flächt aber auch mitunter das Maximum ab (2418984, 2422347, 5763, 6167) oder setzt schon vor dem Maximum ein (2421058, 2739, 3592).

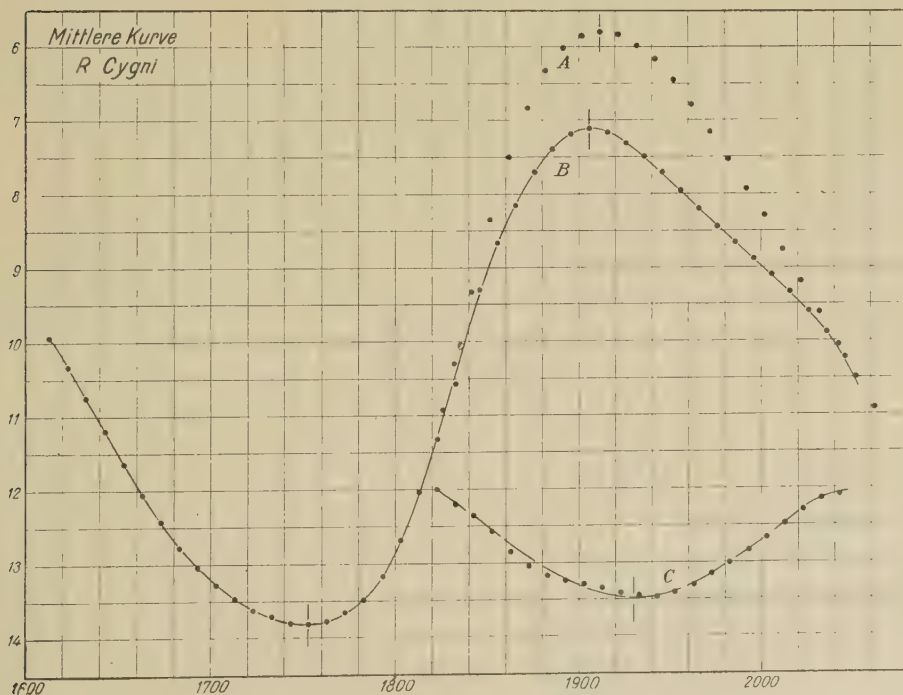


Fig. 2.

TABELLE IV. Die mittlere Kurve.

Phase	$\nu$	Phase	$\nu$	Phase	$\nu$	Phase	$\nu$
$-120^d$	$10.75^m$	$0^d$	$30.80^m$	$+120^d$	$7.83^m$	$+240^d$	$8.83^m$
$-110$	11.21	$+10$	13.77	$+130$	7.48	$+250$	9.06
$-100$	11.65	$+20$	13.67	$+140$	7.24	$+260$	9.29
$-90$	12.06	$+30$	13.48	$+150$	7.13	$+270$	9.53
$-80$	12.43	$+40$	13.17	$+160$	7.13	$+280$	9.80
$-70$	12.76	$+50$	12.68	$+170$	7.26	$+290$	10.19
$-60$	13.04	$+60$	12.04	$+180$	7.44	$+300$	10.62
$-50$	13.28	$+70$	11.24	$+190$	7.67		
$-40$	13.47	$+80$	10.39	$+200$	7.90		
$-30$	13.62	$+90$	9.58	$+210$	8.14		
$-20$	13.73	$+100$	8.84	$+220$	8.37		
$-10$	13.79	$+110$	8.28	$+230$	8.60		

Die mittlere Kurve ist von dieser Störung in analoger Weise beeinflusst worden, wie es s.Z. bei *S Ursae Majoris* gefunden wurde, mit diesem Unterschiede, dass die Kurve dort beim Aufstieg etwas gerader gestreckt wurde, hier aber, wo die Störung später auftritt, beim Abstieg. Beide Sterne haben das Spektrum Se. Ich habe, wie bei *S Ursae Majoris*, auch jetzt die Arbeitshypothese aufgestellt, dass *sämtliche* Maxima einer Störung unterliegen, und den ungestörten Verlauf so zu ziehen mich bemüht, dass die ungestörte Kurve der wirklich beobachteten sowohl im Auf- wie auch im Abstieg gut anschmiegt. Das konnte immer zwanglos geschehen. Natürlich ist eine gewisse Willkür nicht zu vermeiden, und es bleibt auch hier namentlich die Höhe der neuen Kurve etwas unsicher; die Epochen der „ungestörten“ Maxima können aber als ziemlich gut verbürgt gelten. Die Tabelle V enthält eine Zusammenstellung dieser ungestörten Maxima nebst einer Vergleichung mit den Elementen

$$\begin{aligned} R: & 2421928^d + 423^d E \\ \text{und} \quad F: & 2421912 + 423 E + 0^d.42 E^2. \end{aligned}$$

Das grösste Licht wird jetzt im Mittel  $5^m.79 \pm 0^m.113$  (m.F.).

Auch die mittlere Kurve *A* des ungestörten Maximums schliesst sich der Kurve des Minimums wieder gut an (Fig. 2). Für die Schiefe der ungestörten Kurve findet man

$$\frac{M-m}{p} = 0^m.38.$$

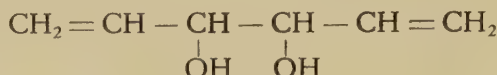




**Chemistry.** — GRINER's *divinylglycol*. By P. VAN ROMBURGH and W. VAN HASSELT.

(Communicated at the meeting of January 30, 1932.)

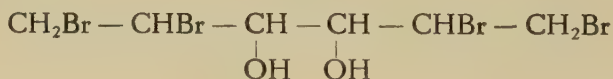
GRINER<sup>1)</sup> has obtained divinylglycol by the reduction of acrolein dissolved in diluted acetic acid with zinc covered with a film of copper. An examination of the formula of this compound,



will show that it contains two identical asymmetric carbon atoms.

The existence of two inactive forms, viz. one racemic and the other by internal compensation, is therefore possible. In order to decide which form is represented by GRINER's glycol, LE BEL tried to obtain an active form by growing moulds in a diluted solution of this glycol, but without success. The solution after the experiment was inactive. GRINER concluded therefore that his compound represents the inactive form by internal compensation.

The glycol combines directly with two molecules of bromine, forming a tetrabromide:



occurring in two forms, melting, according to GRINER, resp. at 96° and 174°.

In fact the *i*-divinylglycol may give three inactive tetrabromides viz. one racemic form and two by internal compensation.

If the above mentioned conclusion of GRINER, concerning the configuration of his glycol, is right, the elimination of the bromine from the two different tetrabromides might be expected to result in the recovering of the original *i*-glycol, which, of course, on combining with bromine would again produce a mixture of both the tetrabromides mentioned above.

If, on the other hand, the original glycol should be a mixture of two isomerides, it would be possible to isolate them.

Many years ago one of the authors (v. R.) made preliminary experiments in order to solve this question.

The tetrabromide (m.p. 174°) was refluxed in absolute ethyl alcohol with zinc dust and the recovered glycol (which we denote by A) without

<sup>1)</sup> Ann. de Chim. [6] 26, 367 (1892).

further purification was treated with bromine according to GRINER's method. The tetrabromide obtained in this reaction had an identical melting point with that of the original bromide. A proof of the presence of the isomeride melting at  $96^{\circ}$  could not be obtained.

It seemed interesting to us first to subject the lower melting tetrabromide to the same reaction, and to isolate the glycols derived from both the isomerides.

The experiments showed, that the glycol (denoted by *B*) derived from the bromide (m.p.  $96^{\circ}$ ) yielded on bromination a tetrabromide with the same melting point without formation of the bromide melting at  $174^{\circ}$ .

On examination, the two glycols (*A*) and (*B*), obtained by elimination of the bromine, appeared to be quite different. The bromide (m.p.  $174^{\circ}$ ) yielded a glycol (*A*) which solidified at  $10^{\circ}$ , the other (*B*) on the contrary, at  $-40^{\circ}$ . The physical constants moreover were quite different.

Presumably they represent resp. the racemic and the inactive form of divinylglycol, unless there have been intermolecular rearrangements.

### *Experimental.*

#### *Preparation of the glycol A.*

A solution of 25 grams of the tetrabromide (m.p.  $174^{\circ}$ ) in 150 c.c. of absolute ethyl alcohol treated with 30 grams of zinc dust was refluxed for six hours. The reaction mixture was filtered and the alcohol distilled under diminished pressure. Water was added to the residue and the mixture treated with sodium carbonate and filtered. The filtrate was extracted with ether. After removal of the ether there remained about 6 grams of the glycol *A* formed in the reaction.

#### *Addition of bromine to glycol A.*

In a two-necked flask, cooled with a mixture of ice and salt and equipped with a mechanical stirrer, the crude glycol, dissolved in 50 c.c. of chloroform, was placed and the stirrer started. Drop by drop bromine was added till the absorption of the bromine stopped. A crystalline white mass separated which was filtered off and dried (weight about 15 grams). The melting point of the crude product was  $150^{\circ}$ . It was washed with benzene and recrystallised from that solvent. The pure product melted at  $172^{\circ}$ .

A tetrabromide with the lower melting point ( $96^{\circ}$ ) could not be separated.

#### *Preparation of the glycol B.*

Using the same technique, 15 grams of the tetrabromide (m.p.  $96^{\circ}$ ) were treated with zinc dust. The glycol *B* formed in this reaction, was dissolved in chloroform and treated with bromine in the manner as described above.

The behaviour of this glycol was quite different from that of glycol *A*.

The chloroform solution did not depose any crystals till the end of the reaction and they only gradually appeared after standing for some time. The melting point of this tetrabromide was  $74^{\circ}$  and on further recrystallisation  $96^{\circ}$ .

The tetrabromide melting at  $174^{\circ}$  could not be demonstrated.

Samples of the glycols *A* and *B* were subjected to fractional distillation. The main fraction showed the following constants :

	Glycol A	Glycol B
B.P. <sup>15mm</sup>	$125^{\circ}$	$125^{\circ}$
$d_{15}^{18}$	1.027	1.016
$n_D^{18}$	1.4822	1.4775
MR <sub>D</sub>	31.66	31.73    Calc. for $C_6H_{10}O_2$ $\sqrt{2}$ 32.
M.P.	$+10^{\circ}$	$-40^{\circ}$

A further investigation of the glycol is to follow.

**Chemistry.** — *Osmosis in systems consisting of water and tartaric acid. I.*

By F. A. H. SCHREINEMAKERS and J. P. WERRE.

(Communicated at the meeting of January 30, 1932.)

### Introduction.

We imagine the composition of a liquid, containing the substances *W* (water) and *X*, represented in the well-known way by a point *a* of the line *WX* (figs. 1 and 2). If we bring an invariant membrane<sup>1)</sup>, absorbing both substances, into this liquid *a*, then it will get a definite *W*- and *X*-amount, which we represent by the length of the line *aa'* and *aa''* (fig. 1). If we give all compositions, beginning with pure *W* (water) and ending with the pure substance *X*, to this liquid *a*, then point *a'* will proceed along a curve *W'a'X* and point *a''* along a curve *Wa''X'*, which curves we call the *W*- and *X*-curves of the membrane.

We may divide these absorption-diagrams into four groups, depending on the *W*- and *X*-curves having a maximum yes or no [figs. 1—4 of these Proceedings 32, 837 (1929)].

- I. Neither of the two curves has a maximum (fig. 1 l.c.).
- II. Only the *W*-curve has a maximum (fig. 2 l.c.).
- III. Only the *X*-curve has a maximum (fig. 3 l.c.).
- IV. Both curves have a maximum (fig. 4 l.c.).

In fig. 1 of this communication we find a diagram I, in fig. 2 a diagram II; in the last case, however, only the *W*-curve has been drawn. the *X*-curve, not drawn, has a shape as given in fig. 1.

<sup>1)</sup> F. A. H. SCHREINEMAKERS, Rec.-Trav. Chim. des Pays-Bas, 50, 883 (1931).



We now shall say that an osmotic system belongs to type I (II, III or IV), when we are able to describe and deduce its osmosis with the aid of the sluice *D.T.* of diagram I (II, III or IV).

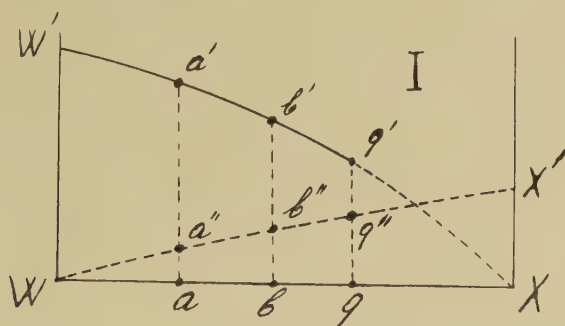


Fig. 1.

Of course it does not follow from the above that the membrane of an osmotic system, belonging e.g. to type I, will now also have a *W*- and an *X*-curve as in diagram I; this is possible, indeed, but not necessary<sup>1)</sup>.

We may attach also quite another meaning to the *W*- and *X*-curve of these diagrams, in which case we no longer pay attention to the absorption by the membrane and consequently not to its sluice *D.T.* either.

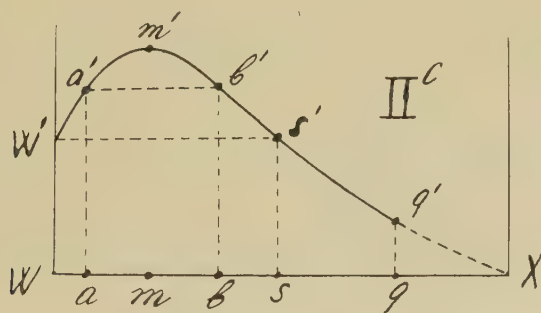


Fig. 2.

To every liquid of the line *WX* namely belongs a point of the *W*- and a point of the *X*-curve; we shall call these points the *W*- and *X*-point of this liquid; e.g. to liquid *a* (fig. 1) belong the *W*-point *a'* and the *X*-point *a''*, to liquid *b* the *W*-point *b'* and the *X*-point *b''*. As  $aa' > bb'$  we shall say that liquid *a* has a higher *W*-point than liquid *b*; as  $aa'' < bb''$  we shall say that liquid *a* has a lower *X*-point than liquid *b*. Besides we shall also say now:

a diagram represents the osmosis of a system schematically, when the phenomena occurring with the osmosis can be described qualitatively and deduced with the aid of the rule:

<sup>1)</sup> F. A. H. SCHREINEMAKERS, l. c.

the water (the substance  $X$ ) diffuses from the liquid with the higher towards the liquid with the lower  $W$ -point ( $X$ -point); when the  $W$ -points ( $X$ -points) of two liquids are situated at the same height, no water ( $X$ ) diffuses.

Here also we shall say now:

an osmotic system belongs to type I (II, III or IV) when we are able to describe its osmosis with the aid of diagram I (II, III or IV).

The  $W$ - and  $X$ -curves of the diagrams have now been given a meaning which is no longer connected with the absorption by the membrane; it also enables us, however, to get a clearer view of the phenomena occurring with the osmosis.

We now take an osmotic system



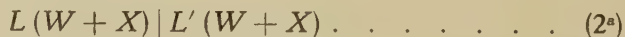
in which the liquids consist of water and tartaric acid. The phenomena which may occur with the osmosis in this system, depend not only upon the concentration of the two liquids, but also upon the nature of the membrane. It appeared namely from our experimental investigation:

1. if we bring a membrane of cellophane into system (1), the system belongs to type I;
2. if we bring a membrane of pig's bladder into system (1), the system belongs to type II.

If in figs 1 and 2 we represent the solution, saturated with solid tartaric acid by point  $q$ , then only the parts of the  $W$ - and  $X$ -curves, situated on the left side of the line  $qq'$ , represent stable states; the stable part  $W'q'$  of the  $W$ -curve has been fully drawn in both figures; the metastable part  $q'X$  shown in a dotted line, may henceforth be left out of consideration.

*Systems with a membrane of cellophane. Type I, fig. 1.*

We now take the osmotic system



in which the tartaric acid has been represented by  $X$ ; for the sake of concentration we shall in this and in the following systems place the liquid with the smaller  $X$ -amount on the left side and consequently that with the larger  $X$ -amount on the right side of the membrane.

If in figs. 1 and 2 we represent these liquids by points of the line  $WX$ , then  $L$  will consequently always be situated on the left side of  $L'$ .

If we bring a membrane of cellophane into this system, then, as we shall see later on, we are able to deduce and describe all phenomena, found with the osmosis in this system, with the aid of fig. 1; consequently this system belongs to type I.

We now imagine the liquids  $L$  and  $L'$  of this system represented in fig. 1 by the points  $a$  and  $b$ . As  $aa' > bb'$ , it follows that liquid  $L$  has a higher  $W$ -point than liquid  $L'$ ; we indicate this by  $w > w'$ . As  $aa'' < bb''$ , it follows that liquid  $L$  has a lower  $X$ -point than  $L'$ ; we represent this by  $x < x'$ . Now we shall represent (2a) by:

$$L(W+X) \left| \begin{array}{c} w > w' \\ x < x' \end{array} \right| L'(W+X) \left\{ \begin{array}{c} \leftarrow X \quad \rightarrow W \end{array} \right\} \dots \dots \dots (2b)$$

As is apparent from fig. 1, this obtains not only for the liquids  $a$  and  $b$ , but for any liquid  $L$  and  $L'$ , provided that, as has been assumed above, liquid  $L$  has a smaller  $W$ -amount than liquid  $L'$ .

As the water diffuses from a liquid with the higher-towards a liquid with the lower  $W$ -point, the water must consequently always flow through the membrane  $\rightarrow$ . As the substance  $X$  also flows from a liquid with the higher-towards a liquid with the lower  $X$ -point, the substance  $X$  must consequently always diffuse  $\leftarrow$ . So the water and the substance  $X$  will always diffuse according to the arrows in (2b).

Consequently the water always diffuses from the liquid with the greater towards the liquid with the smaller  $W$ -amount; the substance  $X$  (viz. the tartaric acid) diffuses from the liquid with the greater towards the liquid with the smaller  $X$ -amount; consequently the two substances here diffuse congruently and positively. In our next communication we shall show that the water can also diffuse incongruently and negatively, when the cellophane is replaced by a pig's bladder.

#### *Systems in which the left-side liquid is invariant.*

As a special case of (2a) or (2b) we first consider the system

$$\text{inv. (Water)} \mid L'(W+X) \left\{ \begin{array}{c} \leftarrow X \quad \rightarrow W \end{array} \right\} \dots \dots \dots (3)$$

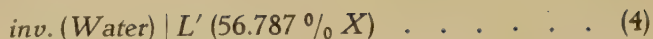
in which on the left side of the membrane we have pure water, which during the entire osmosis is renewed continuously or at short intervals, so that we may practically consider the state on the left side of the membrane as invariant.

It appears from the arrows that the water will now always diffuse  $\rightarrow$  namely from the pure water towards the solution; the tartaric acid diffuses  $\leftarrow$  namely from the solution towards the pure water.

We now take first an osmotic system, in which at the beginning of the osmosis the variable liquid  $L'$  of system (3) contains in procents of weight:

$$43.213\% W + 56.787\% \text{ tartaric acid}$$

we represent this system by:



The data for this system are found in table A. In the first column we find the numbers of the successive determinations, in the second column the time, namely the number of hours passed after the beginning of the osmosis; in the third column we find the composition of the invariant liquid  $L$ , consisting of pure water during the entire osmosis and having, therefore, an  $X$ -amount  $= 0\%$ ; in the last column we find the  $X$ -amount of the variable liquid  $L'$ .

In the fourth column we find sub  $X$  the number of grams of  $X$  and in the fifth column sub  $W$  the number of grams of water, which have passed through the membrane between two successive determinations; the arrows indicate the direction, in which these quantities have diffused. We see that these directions correspond with those of the arrows in system (3).

It appears from Nos 1 and 2 that the  $X$ -amount of the variable liquid  $L'$  had after 6 hours decreased from 56.787 to 52.229 % and that at this time 2.975 gr. of  $X$  had diffused towards the left and 18.020 gr. of water towards the right.

It appears from N<sup>o</sup>. 3 that the  $X$ -amount of the variable liquid had after the beginning of the osmosis decreased to 46.395 % in 15 hours; it follows

TABLE A. System (4).

N <sup>o</sup> .	t	% $X$ of the inv. liq. $L$	Diffused		% $X$ of the var. liq. $L'$
			gr. $X$	gr. $W$	
1	0	0			56.787
			←	→	
2	6		2.975	18.020	52.229
3	15		4.508	26.380	46.395
4	24		4.256	23.242	41.895
5	36		4.942	27.061	37.321
6	48		5.444	25.213	33.421
7	65		6.678	31.806	29.132

from Nos 2 and 3 together that between these two determinations (consequently in  $15 - 6 = 9$  hours) 4.508 gr. of  $X$  had diffused towards the left and 26.380 gr. of water towards the right.

From this follows also that in 15 hours counting from the beginning of the osmosis

$$2.975 + 4.508 = 7.483 \text{ gr. } X (\text{tartaric acid})$$



in all had diffused towards the left and

$$18.020 + 26.380 = 44.400 \text{ gr. } W (\text{Water})$$

in all towards the right.

It follows from the last determination N<sup>o</sup>. 7 that the  $X$ -amount of the variable liquid  $L'$  had decreased to 29.132 % in 65 hours counting from the beginning of the osmosis; we find that now 28.803 gr. of  $X$  in all had diffused towards the left and 151.722 gr. of  $W$  towards the right.

As is shown by table A, the osmosis of system (4) stopped, when the variable liquid  $L'$  still contained 29.132 % of tartaric acid; in order to become acquainted with the subsequent course of the osmosis, we now take the system

$$\text{inv. (Water)} | L' (34.628 \% X) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which at the beginning of the osmosis the variable liquid contains

$$65.372 \% W + 34.628 \% \text{ tartaric acid.}$$

From the determinations<sup>1)</sup>, which were carried on until the variable liquid contained only 0.008 % of  $X$ , it now appears that also during this entire osmosis the substance  $X$  and the water diffuse according to the arrows of system (3).

From this table (l.c.) it appears among other things that the  $X$ -amount of the variable liquid had decreased to 31.576 % in 9 hours counting from the beginning of the osmosis and that then 4.726 gr. of  $X$  had diffused towards the left and 19.082 gr. of water towards the right.

In 160 hours the  $X$ -amount of the variable liquid had decreased to 7.978 %, then 51.923 gr. of  $X$  had diffused towards the left and 197.645 gr. of water towards the right.

In 1053 hours the  $X$ -amount of the variable liquid decreased to 0.008 % and 73.801 gr. of  $X$  had in all diffused towards the left and 311.062 gr. of  $W$  towards the right.

We now take the osmotic system

$$\text{inv. (Water)} | L'_q (W + X) + \text{solid } X \quad . \quad . \quad . \quad . \quad . \quad (6)$$

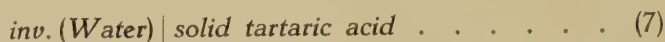
in which the right side liquid has been saturated with solid tartaric acid; in fig. 1, therefore, it is represented by the point  $q$ .

As for this system the arrows of system (2b) or (3) obtain also, the liquid  $L'$  will give off the substance  $X$  and take in water; so in this

1) J. P. WERRE. Diss. Leiden 1931, table VI, pag. 33; this table in which 22 determinations occur and in which the tartaric acid has been indicated by  $Z$ , has practically been arranged in a similar way as that of table A.

system two factors cooperate to cause the disappearance of the solid substance  $X$ ; as soon as all the solid substance has disappeared, this system passes into system (3).

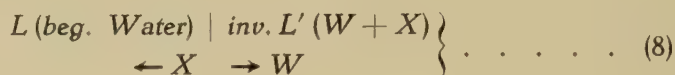
If in system (6) we omit the liquid, we get a system



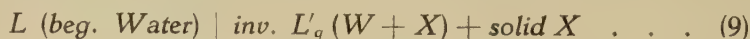
Let us now imagine that at a certain moment a very small quantity of water diffuses, then on the right side some saturated solution will form. As system (7) then passes into (6), the water-diffusion will now, as we saw before, continue towards the right and the substance  $X$  will diffuse towards the left. From this it follows, as we have also learned experimentally, that the solid tartaric acid in system (7) will deliquesce and dissolve.

*Systems in which the right side liquid is invariant.*

As an other special case of system (2a) or (2b) we now take a system



in which an invariant liquid is found this time on the right side of the membrane. On the left side of the membrane is a variable liquid  $L$ , consisting at the beginning of the osmosis of pure water. In order to determine the osmosis in such a system (8), we took the system:



in which the liquid  $L'$  is saturated with solid  $X$ ; if we take care that a large quantity of solid tartaric acid is present all the time, then liquid  $L'$  will be practically invariant. This liquid represented in fig. 1 by point  $q$  contains

$\pm 42.5\%$  of  $W$  and  $\pm 57.5\%$  of tartaric acid.

We now represent this system by:



The data, concerning the osmosis in this system are found in table  $B$ , which has been arranged in a similar way as that of table  $A$ ; the liquid  $L$  (third column) now is variable, however, and the liquid  $L'$  (last column) invariant.

It appears from the arrows of this table  $B$  that the substance  $X$  and the

TABLE B. System (10).

No.	<i>t</i>	% <i>X</i> of the var. liq. <i>L</i>	Diffused		% <i>X</i> of the inv. liq. <i>L'</i>
			gr. <i>X</i>	gr. <i>W</i>	
1	0	0			± 57.5
			←	→	
2	3	0.425	1.611	8.122	
3	8	1.145	2.455	13.431	
4	16	2.397	3.745	18.115	
5	28	5.089	6.762	33.468	
6	40	7.651	5.345	26.498	
7	49	8.684	2.988	16.361	
8	73	12.170	8.620	47.951	
9	93	15.149	5.929	34.101	
10	111	17.633	4.148	24.577	
11	131	21.240	5.075	30.348	
12	164	28.858	7.252	50.958	
13	204	37.301	4.495	41.170	
14	248	40.325	2.391	28.547	
15	291	43.029	2.464	24.156	
16	362	46.219	1.600	26.508	
17	457	49.853	1.811	26.083	
18	625	52.998	0.050	21.141	
19	888	55.631	1.632	14.512	

water diffuse also in this system during the entire osmosis in the way indicated by the arrows in system (2*b*).

From this table *B* it besides appears among other things that the *X*-amount of the variable liquid *L*, consisting of pure water at the beginning of the osmosis, had increased to 0.425 % after 3 hours and that then 1.611 gr. of *X* had diffused towards the left and 8.122 gr. of water towards the right.

After 111 hours the *X*-amount of the variable liquid had increased to 17.633 % and 41.603 gr. of *X* had diffused towards the left and 222.624 gr. of water towards the right.

After 888 hours the *X*-amount of the variable liquid had increased to 55.631 % and had consequently almost come up to that of the saturated

solution  $L'$ ; then 68.373 gr. of  $X$  had gone towards the left and 486.047 gr. of water towards the right.

*The diffusing mixture.*

Above we have seen that in system (2a) or (2b) and in all systems deduced from them the substance  $X$  and the water diffuse during the entire osmosis in the way indicated by the arrows in (2b). We now represent this by

$$\leftarrow \alpha \cdot X \quad \rightarrow \gamma W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which  $\alpha$  and  $\gamma$  indicate the small quantities of  $X$  and  $W$ , flowing through the membrane between the moments  $t$  and  $t + dt$ . It appears from the tables  $A$ ,  $B$  and VI (l.c.) that during the entire osmosis  $\alpha < \gamma$ .

So in this time  $dt$  the quantity of the left side liquid  $L$  decreases with a positive quantity  $\gamma - \alpha$  and that of the right side liquid  $L'$  increases with the same quantity  $\gamma - \alpha$ . From this follows that we now may say also: liquid  $L$  gives off and liquid  $L'$  takes in  $\gamma - \alpha$  quantities of a mixture with the composition:

$$x_0 X + (1 - x_0) W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which

$$x_0 = \frac{-\alpha}{\gamma - \alpha} \quad \text{and} \quad 1 - x_0 = \frac{\gamma}{\gamma - \alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

so that  $x_0$  is negative and consequently  $1 - x_0$  positive, and larger than 1; before<sup>1)</sup> we have called this mixture the diffusing mixture.

We can also represent the composition of this diffusing mixture by a point  $d$ , not drawn in fig. 1, of the line  $WX$ . As, however, this mixture is not a liquid existing in reality (this mixture namely has a negative  $X$ -amount and a  $W$ -amount larger than 1), this point will of course not be situated between the points  $W$  and  $X$ ; it is easy to find that this point  $d$  must be situated to the left of point  $W$ , namely somewhere on the prolongation of line  $WX$ . The length of line  $dW$  then represents the negative  $X$ -amount and the length of line  $dX$  the positive  $W$ -amount of this mixture.

Later on we shall refer again to the diffusing mixture and its movement during the osmosis.

(To be continued.)

*Leiden, Lab. of Inorg. Chemistry.*

<sup>1)</sup> F. A. H. SCHREINEMAKERS. Verslagen K. Ak. v. W., 36, 1103 (1927). These Proceedings 30, 1095 (1927).



**Mathematics.** — *Tafel der primitiven gleichschenkligen Dreiecke mit rationalen Winkelhalbierenden und mit Schenkeln kleiner als 160000.* Von J. G. VAN DER CORPUT.

(Communicated at the meeting of January 30, 1932.)

Ein Dreieck heisst primitiv, wenn die Längen der Seiten ganze Zahlen mit einem grössten gemeinsamen Teiler gleich 1 sind. In einer vorigen Mitteilung <sup>1)</sup> habe ich bewiesen:

Bezeichnen  $m$  und  $n$  zwei natürliche, teilerfremde Zahlen verschiedener Parität mit  $m > n$ , so ist das gleichschenklige Dreieck  $ABC$  mit den Seiten

$$a = b = (m^2 + n^2)^2 \quad \text{und} \quad c = \pm 2(m^2 - 2mn - n^2)(m^2 + 2mn - n^2)$$

ein primitives Dreieck mit rationalen Winkelhalbierenden, und auf diese Art findet man alle gleichschenkligen primitiven Dreiecke mit rationalen Winkelhalbierenden.

Da 63 verschiedene Paare natürlicher teilerfremder Zahlen  $m$  und  $n$  verschiedener Parität mit  $m > n$  und  $m^2 + n^2 < 400$  existieren, gibt es 63 verschiedene primitive gleichschenklige Dreiecke mit rationalen Winkelhalbierenden und mit Schenkeln  $< 160000$ . Diese Dreiecke  $D_1, D_2, \dots, D_{63}$  (nach der Grösse des Schenkels geordnet) sind in der folgenden Tafel aufgenommen; hierin bezeichnet  $a$  den Schenkel,  $c$  die Basis,  $h$  die Höhe und  $A$  den Basiswinkel des Dreieckes. Zum Beispiel  $D_1$  ist das primitive gleichschenklige Dreieck mit den Seiten 25, 25, 14 und mit der Höhe  $24.1 = 24$ ; in diesem Dreieck haben die inneren bzw. äusseren Halbierenden der Basiswinkel die Längen

$$\frac{2bc}{b+c} \cos \frac{1}{2} A = \frac{2 \cdot 25 \cdot 14}{25 + 14} \cdot \frac{4}{5} = \frac{560}{39},$$

bzw.

$$\frac{2bc}{b-c} \sin \frac{1}{2} A = \frac{2 \cdot 25 \cdot 14}{25 - 14} \cdot \frac{3}{5} = \frac{420}{11}.$$

Bezeichnet  $qD_v$  ( $v=1, 2, \dots, 63$ ), wo  $q$  eine positive Zahl ist, das Dreieck, dessen Seiten  $q$ -mal so gross sind wie die Seiten von  $D_v$ , dann haben die zwei Dreiecke  $5D_1$  und  $D_2$  dieselbe Höhe 5.24. Werden diese zwei Dreiecke so aufeinander gelegt, dass diese Höhen zusammenfallen, dann entstehen zwei neue Dreiecke, die ich mit  $D_2 \pm 5D_1$  bezeichnen werde, mit den Seiten 169, 120 und  $119 \pm 35$  und mit rationalen Winkel-

<sup>1)</sup> Diese Proceedings, 34, S. 1390.

TAFEL

	$m$	$n$	$\sqrt{a}$	$\frac{1}{2}c$	$\frac{1}{24}h$	$tg \frac{1}{4}A$	$\sqrt{a} \cos \frac{1}{2}A$	$\sqrt{a} \sin \frac{1}{2}A$
1	2	1	5	7	1	1 : 3	4	3
2	3	2	13	119	5	1 : 5	12	5
3	4	1	17	161	2. 5	1 : 4	15	8
4	4	3	25	527	2. 7	1 : 7	24	7
5	5	2	29	41	5. 7	2 : 5	21	20
6	6	1	37	1081	5. 7	1 : 6	35	12
7	5	4	41	1519	2. 3. 5	1 : 9	40	9
8	7	2	53	1241	3. 5. 7	2 : 7	45	28
9	6	5	61	3479	5. 11	1 : 11	60	11
10	7	4	65	2047	2. 7. 11	3 : 11	56	33
11	8	1	65	3713	2 <sup>2</sup> . 3. 7	1 : 8	63	16
12	8	3	73	721	2 <sup>2</sup> . 5. 11	3 : 8	55	48
13	9	2	85	4633	3. 7. 11	2 : 9	77	36
14	7	6	85	6887	7. 13	1 : 13	84	13
15	8	5	89	4879	2 <sup>2</sup> . 5. 13	3 : 13	80	39
16	9	4	97	959	2. 3. 5. 13	5 : 13	72	65
17	10	1	101	9401	3. 5. 11	1 : 10	99	20
18	10	3	109	4681	5. 7. 13	3 : 10	91	60
19	8	7	113	12319	2 <sup>2</sup> . 5. 7	1 : 15	112	15
20	11	2	125	11753	3. 11. 13	2 : 11	117	44
21	11	4	137	3281	2. 5. 7. 11	4 : 11	105	88
22	12	1	145	19873	2. 11. 13	1 : 12	143	24
23	9	8	145	20447	2 <sup>2</sup> . 3. 17	1 : 17	144	17
24	10	7	149	16999	5. 7. 17	3 : 17	140	51
25	11	6	157	10199	5. 11. 17	5 : 17	132	85
26	12	5	169	239	2. 5. 7. 17	7 : 17	120	119
27	13	2	173	24521	5. 11. 13	2 : 13	165	52
28	10	9	181	32039	3. 5. 19	1 : 19	180	19
29	13	4	185	12593	2. 3. 13. 17	4 : 13	153	104
30	11	8	185	27727	2 <sup>2</sup> . 11. 19	3 : 19	176	57
31	12	7	193	19199	2. 5. 7. 19	5 : 19	168	95
32	14	1	197	37241	5. 7. 13	1 : 14	195	28

TAFEL (Fortsetzung).

	$m$	$n$	$\sqrt{a}$	$\frac{1}{2}c$	$\frac{1}{24}h$	$tg \frac{1}{4}A$	$\sqrt{a} \cos \frac{1}{2}A$	$\sqrt{a} \sin \frac{1}{2}A$
33	13	6	205	6647	7. 13. 19	7:19	156	133
34	14	3	205	27913	7. 11. 17	3:14	187	84
35	14	5	221	9641	3. 5. 7. 19	5:14	171	140
36	11	10	221	47959	5. 7. 11	1:21	220	21
37	15	2	229	45241	5. 13. 17	2:15	221	60
38	13	8	233	32239	2 <sup>2</sup> . 5. 7. 13	5:21	208	105
39	15	4	241	29281	2. 5. 11. 19	4:15	209	120
40	16	1	257	64001	2 <sup>3</sup> . 5. 17	1:16	255	32
41	16	3	265	51793	2 <sup>3</sup> . 13. 19	3:16	247	96
42	12	11	265	69167	2. 11. 23	1:23	264	23
43	13	10	269	62839	5. 13. 23	3:23	260	69
44	14	9	277	50279	3. 5. 7. 23	5:23	252	115
45	16	5	281	27761	2 <sup>3</sup> . 5. 7. 11	5:16	231	160
46	15	8	289	31679	2 <sup>2</sup> . 5. 7. 23	7:23	240	161
47	17	2	293	76601	5. 17. 19	2:17	285	68
48	16	7	305	7327	2 <sup>3</sup> . 3. 7. 23	9:23	224	207
49	17	4	305	56033	2. 7. 13. 17	4:17	273	136
50	13	12	313	96719	2. 5 <sup>2</sup> . 13	1:25	312	25
51	14	11	317	89239	5 <sup>2</sup> . 7. 11	3:25	308	75
52	17	6	325	22393	11. 17. 23	6:17	253	204
53	18	1	325	103033	3. 17. 19	1:18	323	36
54	16	9	337	52319	2 <sup>3</sup> . 3. 5 <sup>2</sup> . 7	7:25	288	175
55	18	5	349	57001	3. 5. 13. 23	5:18	299	180
56	17	8	353	23359	2 <sup>2</sup> . 3. 5 <sup>2</sup> . 17	9:25	272	225
57	19	2	365	121673	7. 17. 19	2:19	357	76
58	14	13	365	131767	3 <sup>2</sup> . 7. 13	1:27	364	27
59	18	7	373	12121	3. 5 <sup>2</sup> . 7. 11	7:18	275	252
60	16	11	377	105679	2 <sup>3</sup> . 3 <sup>2</sup> . 5. 11	5:27	352	135
61	19	4	377	95921	2. 5. 19. 23	4:19	345	152
62	17	10	389	79879	3 <sup>2</sup> . 5. 7. 17	7:27	340	189
63	19	6	397	53641	5 <sup>2</sup> . 13. 19	6:19	325	228

halbierenden. Wie ich bewiesen habe<sup>1)</sup>, ergibt jedes Paar der Dreiecke  $D_1, D_2, \dots, D_{63}$  auf diese Art zwei neue Dreiecke mit rationalen Winkelhalbierenden. Ich erwähne hier nur sechs Beispiele, wo  $c$  die Basis,  $h$  die Höhe bezeichnet.

	$a$	$b$	$c$	$\frac{1}{24}h$	$\cos \frac{1}{2}A$	$\sin \frac{1}{2}A$	$\cos \frac{1}{2}B$	$\sin \frac{1}{2}B$	$\cos \frac{1}{2}C$	$\sin \frac{1}{2}C$
$D_2 - 5D_1$	125	169	84	5	12:13	5:13	3:5	4:5	63:65	16:65
$D_2 + 5D_1$	125	169	154	5	12:13	5:13	4:5	3:5	56:65	33:65
$2D_2 - D_3$	289	338	77	10	12:13	5:13	8:17	15:17	220:221	21:221
$2D_2 + D_3$	289	338	399	10	12:13	5:13	15:17	8:17	171:221	140:221
$D_7 - 3D_3$	867	1681	1036	30	40:41	9:41	8:17	15:17	672:697	185:697
$D_7 + 3D_3$	867	1681	2002	30	40:41	9:41	15:17	8:17	455:697	528:697

<sup>1)</sup> Diese Proceedings, 34, S. 1394.

**Mathematics.** — *On the Solution of the Matrix Equation  $AX + XB = C$ .*

By D. E. RUTHERFORD. (Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of January 30, 1932.)

I. In this problem  $A$ ,  $B$  and  $C$  are given matrices and it is required to find  $X$ , or rather, to find the elements of  $X$  in terms of the elements of  $A$ ,  $B$  and  $C$ . A solution is possible only if  $A$  and  $B$  are square matrices, let us say of orders  $n$  and  $m$  respectively, and when  $C$  is a conformable matrix of  $n$  rows and  $m$  columns. It follows that  $X$  also must have  $n$  rows and  $m$  columns.

When  $PX = XQ$ ,  $X$  is called a *commutant* of  $P$  and  $Q$ , and is often written  $X = (P, Q)$ . It is a fundamental fact that this commutant can only be the null matrix, unless the matrices  $P$  and  $Q$  have at least one latent root in common. When common latent roots appear, then the general  $X$  is nonzero and contains arbitrary parameters. (Cf. e. g. TURNBULL and AITKEN, *Canonical Matrices*, (Glasgow, 1932) Chap. X). As may be suspected, our problem presents similar features. If  $C = 0$ , then evidently  $X = (A, -B)$  is the commutant of  $A$  and  $-B$ , two matrices whose latent roots will be denoted by  $\lambda_i, -\mu_j$ . Uniqueness or otherwise of the solution  $X$  will depend on whether  $\lambda_i$  is equal to  $-\mu_j$  or not; in the case of uniqueness (IV below) when  $\lambda_i + \mu_j = 0$ ,  $X$  will however, not be zero.



We shall first consider the case where  $A$  and  $B$  are in the classical canonical form. We therefore write

$$A = \begin{bmatrix} A_1 & & \\ & A_2 & \\ & & \ddots \\ & & & A_p \end{bmatrix} \text{ and } B = \begin{bmatrix} B_1 & & \\ & B_2 & \\ & & \ddots \\ & & & B_q \end{bmatrix};$$

$$\text{where } A_i = \begin{bmatrix} \lambda_i & 1 & & \\ & \lambda_i & 1 & \\ & & \ddots & \ddots \\ & & & 1 & \\ & & & & \lambda_i \end{bmatrix} \text{ and } B_j = \begin{bmatrix} \mu_j & 1 & & \\ & \mu_j & 1 & \\ & & \ddots & \ddots \\ & & & 1 & \\ & & & & \mu_j \end{bmatrix},$$

all elements not indicated being zero, and where neither  $\lambda_1, \lambda_2, \dots, \lambda_p$  nor  $\mu_1, \mu_2, \dots, \mu_q$  are necessarily all distinct. We now split up  $C$  and  $X$  in the following manner,

$$X = \begin{bmatrix} X_{11}, X_{12}, \dots, X_{1q} \\ X_{21}, X_{22}, \dots, X_{2q} \\ \vdots \\ X_{p1}, X_{p2}, \dots, X_{pq} \end{bmatrix} \text{ and } C = \begin{bmatrix} C_{11}, C_{12}, \dots, C_{1q} \\ C_{21}, C_{22}, \dots, C_{2q} \\ \vdots \\ C_{p1}, C_{p2}, \dots, C_{pq} \end{bmatrix}$$

where the submatrices  $X_{ij}$  and  $C_{ij}$  have the same number of rows as  $A_i$ , and the same number of columns as  $B_j$ .

II. The submatrix  $X_{ij}$  is now given by the equation

$$A_i X_{ij} + X_{ij} B_j = C_{ij}.$$

Let  $A_i$  and  $B_j$  be of orders  $s$  and  $t$  respectively; then we write

$$X_{ij} = \begin{bmatrix} x_{11}, x_{12}, \dots, x_{1s} \\ \vdots \\ x_{t1}, x_{t2}, \dots, x_{ts} \end{bmatrix} \text{ and } C_{ij} = \begin{bmatrix} c_{11}, c_{12}, \dots, c_{1s} \\ \vdots \\ c_{t1}, c_{t2}, \dots, c_{ts} \end{bmatrix}.$$

The equations for the elements  $x$  are easily shown to be

$$\left. \begin{aligned} \lambda_i x_{k,l} + x_{k+1,l} + x_{k,l-1} + \mu_j x_{k,l} &= c_{k,l}, & (k < t; l > 1) \\ \lambda_i x_{k,1} + x_{k+1,1} + \mu_j x_{k,1} &= c_{k,1}, & (k < t) \\ \lambda_i x_{t,l} + x_{t,l-1} + \mu_j x_{t,l} &= c_{t,l}, & (l > 1) \\ \lambda_i x_{t,1} + \mu_j x_{t,1} &= c_{t,1}. \end{aligned} \right\} \quad \dots \quad (1)$$

These may be rewritten as

$$x_{t,1} = \frac{c_{t,1}}{\lambda_i + \mu_j},$$

$$x_{t,l} = \frac{c_{t,l} - x_{t,l-1}}{\lambda_i + \mu_j}, \quad (l > 1),$$

$$x_{k,1} = \frac{c_{k,1} - x_{k+1,1}}{\lambda_i + \mu_j}, \quad (k < t),$$

$$x_{k,l} = \frac{c_{k,l} - x_{k+1,l} - x_{k,l-1}}{\lambda_i + \mu_j}, \quad (k < t; l > 1).$$

III. We shall first consider the case where  $\lambda_i + \mu_j \neq 0$ . In this case every element of  $X_{ij}$  is exactly determined from the last equations. Indeed any element  $x$  is equal to the corresponding  $c$ , minus the  $x$  element immediately on the left, minus the  $x$  element immediately below, all divided by  $\lambda_i + \mu_j$ . Hence any letter  $c_{k,l}$  will appear in the  $kl$ th place in  $X_{ij}$  and also in every place to the right of, and above the  $kl$ th place; also the coefficient of  $c_{k,l}$  in the  $uv$ th place of  $X_{ij}$  ( $u < k, v > l$ ) is

$$(-1)^{u+v-k-l} \binom{u+v-k-l}{u-k} (\lambda_i + \mu_j)^{k+l-u-v-1}.$$

IV. Let us now consider the case where  $\lambda_i + \mu_j = 0$ . If  $c_{t,1} \neq 0$ , then  $x_{t,1}$  and every other element  $x$  of  $X_{ij}$  can easily be shown to be infinite. Similarly, if any  $x_{r,w}$  of  $X_{ij}$  be infinite, every element above and to the right of  $x_{r,w}$  must be infinite. If, however,  $c_{t,1} = 0$  a finite solution may exist, for then will  $x_{t,1}$  be arbitrary; but  $x_{t,2}$  will be infinite unless  $c_{t,2} - x_{t,1} = 0$ , so that if we take  $x_{t,1} = c_{t,2}$ , then  $x_{t,2}$  is arbitrary.

Now if  $t < s$ , we may proceed in this manner and obtain  $x_{t,s}$  arbitrary by putting  $x_{t,l} = c_{t,l+1}$  where  $l < s$ . If  $x_{t-1,1}$  be not infinite, then must

$$c_{t-1,1} - x_{t,1} = c_{t-1,1} - c_{t-1,2} = 0,$$

and, proceeding as before, we have  $x_{t-1,s}$  arbitrary by putting

$$x_{t-1,l} = c_{t-1,l+1} - x_{t,l+1}.$$

In the same way, if  $x_{t-h,1}$  be not infinite then must

$$c_{t-h,1} - c_{t-h+1,2} + c_{t-h+2,3} - \dots (-1)^h c_{t,h+1} = 0 \quad (h < t < s). \quad (2)$$

Also we have  $x_{t-h,s}$  arbitrary by taking

$$x_{t-h,l} = c_{t-h,l+1} - x_{t-h+1,l+1} \quad (l < s).$$

In this way we can obtain every element  $x$  in terms of the  $c_{ij}$  and of  $t$  arbitrary parameters.

If  $t > s$  then we proceed in a similar manner, but we take the  $s$  arbitrary elements  $x_{1,1}, x_{1,2}, \dots, x_{1,s}$  instead of  $x_{1,s}, x_{2,s}, \dots, x_{t,s}$ .

The same relations between the elements  $c$  will hold, but in equation (2) the values of  $h$  are given by  $h < s < t$ . The equations for the elements  $x$  in this case will be

$$x_{k,1} = c_{k-1,1}; \quad x_{k,l} = c_{k-1,l} - x_{k-1,l-1} \quad (k > 1; l > 1).$$

Thus, if  $\lambda_i + \mu_j = 0$ , a finite solution exists if, and only if, the following relations hold for the elements  $c$ ;

$$\left. \begin{aligned} c_{t,1} &= 0, \\ c_{t-1,1} - c_{t,2} &= 0, \\ c_{t-2,1} - c_{t-1,2} + c_{t,3} &= 0, \\ &\dots \end{aligned} \right\} \dots \quad (3)$$

the last equation of this series being

$$c_{1,1} - c_{2,2} + c_{3,3} - \dots (-)^{t-1} c_{t,t} = 0, \text{ if } s > t,$$

or

$$c_{t-s+1,1} - c_{t-s+2,2} - \dots (-)^{s-1} c_{t,s} = 0, \text{ if } s < t.$$

The solution is then of the form

$$\left[ \begin{array}{ccccccc} c_{1,2} - c_{2,3} + \dots (-)^{t-1} c_{t,t+1}, & \dots, & c_{1,s-1} - c_{2,s} + a_{t-2}, & c_{1,s} - a_{t-1}, & a_t \\ c_{2,2} - c_{3,3} + \dots (-)^{t-2} c_{t,t}, & \dots, & c_{2,s-1} - c_{3,s} + a_{t-3}, & c_{2,s} - a_{t-2}, & a_{t-1} \\ \dots & \dots & \dots & \dots & \dots \\ c_{t-1,2} - c_{t,3} & \dots, & c_{t-1,s-1} - c_{t,s}, & c_{t-1,s} - a_1, & a_2 \\ c_{t,2} & \dots, & c_{t,s-1}, & c_{t,s} & a_1 \end{array} \right] \quad (4)$$

or

$$\left[ \begin{array}{ccccccc} b_1, & b_2, & \dots, & b_{s-1}, & & b_s \\ c_{1,1}, & c_{1,2} - b_1, & \dots, & c_{1,s-1} - b_{s-2}, & & c_{1,s} - b_{s-1} \\ c_{2,1}, & c_{2,2} - c_{1,1}, & \dots, & c_{2,s-1} - c_{1,s-2} + b_{s-3}, & & c_{2,s} - c_{1,s-1} + b_{s-2} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ c_{t-1,1}, & c_{t-1,2} - c_{t-2,1}, & \dots, & c_{t-1,s-1} - \dots (-)^{s-2} c_{t-s+1,1}, & & c_{t-1,s} - c_{t-2,s-1} + \\ & & & & & + \dots (-)^{s-1} c_{t-s,1} \end{array} \right]$$

according as  $s$  is greater or less than  $t$ , where the elements  $a$  and  $b$  are arbitrary parameters.

V. We have now obtained a solution of the equation

$$A_i X_{ij} + X_{ij} B_j = C_{ij}.$$

Solving this equation for all values of  $i$  and  $j$  we obtain every submatrix  $X_{ij}$ ; and building these together we arrive at the solution of  $AX + XB = C$ , where  $A$  and  $B$  are in the classical form. If  $A$  and  $B$  be not already in the classical canonical form, then let  $A = H^{-1} R H$  and let  $B = K^{-1} S K$ , where  $H$  and  $K$  are nonsingular and where  $R$  and  $S$  are in the classical form, so that  $H A H^{-1} = R$  and  $K B K^{-1} = S$ .

But we can find a solution  $Y$  of  $R Y + Y S = D$

$$\text{or of } H A H^{-1} Y + Y K B K^{-1} = D$$

$$\text{or of } A H^{-1} Y K + H^{-1} Y K B = H^{-1} D K.$$

Hence if we choose  $H^{-1} D K = C$  or  $D = H C K^{-1}$ , then  $X = H^{-1} Y K$  is solution of  $AX + XB = C$ . Thus a finite solution to this equation always exists provided that no latent root of  $A$  is equal to the negative of a latent root of  $B$ ; or if this be so, provided that the relations (3) hold. In particular, no finite solution will exist if both the matrices  $A$  and  $B$  be singular.

VI. If every element of  $C_{ij}$  is zero, then so is every element of  $X_{ij}$  unless  $\lambda_i + \mu_j = 0$ . If this be the case then all the equations (2) are satisfied and hence a finite solution exists. By deleting all the elements  $c$  from the matrices (4), we obtain the solution of

$$A_i X_{ij} + X_{ij} B_j = 0 \quad (\lambda_i + \mu_j = 0).$$

Building up the submatrices  $X_{ij}$  in the same way as before, we have the solution of

$$A X + X B = 0.$$

VII. We shall conclude by giving a simple illustration of the foregoing methods. We wish to find the value of  $X$  for which  $AX + XB = C$  where

$$A = \begin{bmatrix} 1 & 0 & -1 & 0 \\ 1 & 2 & 0 & 0 \\ 1 & 0 & 3 & 0 \\ 0 & 0 & 0 & 2 \end{bmatrix}, \quad B = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ -4 & -3 & 0 & 0 \\ -12 & -5 & -4 & 4 \end{bmatrix}, \quad \text{and } C = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Now  $A = H R H^{-1}$  and  $B = K S K^{-1}$  where

$$H = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad R = \begin{bmatrix} 2 & 1 & 0 & 0 \\ 0 & 2 & 1 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 2 \end{bmatrix}, \quad K = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 4 & 3 & 2 & 1 \end{bmatrix},$$



$$\text{and } S = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1 \\ 0 & 0 & 0 & 2 \end{bmatrix}; \text{ also } H^{-1}CK = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & -1 & 0 \\ 4 & 3 & 2 & 1 \end{bmatrix} = D$$

Here the latent roots of  $A$  are  $2, 2, 2, 2$  and those of  $-B$  are  $-2, -2, -1, -1$ . Hence none are common and  $X$  is therefore unique.

The matrices  $R$ ,  $S$  and  $D$  are now partitioned into submatrices in the appropriate manner, as is shown by means of the dotted lines: and we proceed to solve the equation  $RY + YS = D$ . Let  $Y$  be  $\begin{bmatrix} Y_{11} & Y_{12} \\ Y_{21} & Y_{22} \end{bmatrix}$ , then we must have

$$Y_{11} = \begin{bmatrix} -\frac{1}{3^2} - \frac{1}{3^3}, \frac{1}{3} + \frac{2}{3^3} + \frac{3}{3^4} \\ \frac{1}{3} + \frac{1}{3^2}, -\frac{1}{3^2} - \frac{2}{3^3} \\ -\frac{1}{3}, +\frac{1}{3^2} \end{bmatrix}, \quad Y_{12} = \begin{bmatrix} -\frac{1}{4^3}, +\frac{3}{4^4} \\ +\frac{1}{4^2}, -\frac{2}{4^3} \\ -\frac{1}{4}, +\frac{1}{4^2} \end{bmatrix},$$

$$Y_{21} = \begin{bmatrix} 4\frac{1}{3}, 3\frac{1}{3} - 4\frac{1}{3^2} \end{bmatrix}, \quad Y_{22} = \begin{bmatrix} 2\frac{1}{4}, \frac{1}{4} - 2\frac{1}{4^2} \end{bmatrix}.$$

Hence the solution is  $X = HYK^{-1}$  or

$$X = \begin{bmatrix} \frac{1}{3} + \frac{1}{3^2} + \frac{2}{4^2}, -\frac{1}{3^2} - \frac{2}{3^3} + \frac{6}{4^3}, \frac{2}{4^2}, -\frac{2}{4^3} \\ -\frac{1}{3^2} - \frac{1}{3^3} - \frac{3}{4^3}, \frac{1}{3} + \frac{1}{3^2} + \frac{9}{4^4}, -\frac{1}{4^3} - \frac{6}{4^4}, \frac{3}{4^4} \\ -\frac{1}{3^2} + \frac{2}{4^2}, \frac{2}{3^3} + \frac{3}{4^2} - \frac{6}{4^3}, \frac{1}{4}, -\frac{1}{4^2} + \frac{2}{4^3} \\ \frac{4}{3} - \frac{1}{2}, 1 - \frac{4}{3^2} - \frac{3}{4} + \frac{6}{4^2}, \frac{1}{4}, \frac{1}{4} - \frac{2}{4^2} \end{bmatrix}.$$


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**Mathematics.** — *Über die Matrixgleichung  $AX + XB = C$ .* Von  
R. WEITZENBÖCK.

(Communicated at the meeting of January 30, 1932.)

§ 1.

Im Anschlusse an obige Mitteilung des Herrn RUTHERFORD über die Lösung der Matrixgleichung  $AX + XB = C$  will ich auf die Möglichkeit einer „reinen“ Lösung hinweisen. Dabei verstehe ich unter einer „reinen“ Lösung einen Ausdruck  $X = f(\xi, \eta, \zeta, \dots)$ , in welchem  $f$  eine algebraische Funktion ist, deren Argumente  $\xi, \eta, \zeta, \dots$  die Koeffizientenmatrizes  $A, B, \dots$  (und allenfalls deren Transponierten  $A', B', \dots$ ) sind. Die Koeffizienten in  $f$  sollen gewöhnliche komplexe Zahlen oder auch affine Invarianten der Matrices  $A, B, \dots$  sein. Überdies soll eine reine Lösung erhalten werden können, ohne dass man auf die Elemente der Matrices  $A, B, X, \dots$  selbst zurückgeht.

Die obige, durch Herrn RUTHERFORD gegebene Lösung ist nicht-rein. Dasselbe gilt von der durch RICHARDSON<sup>1)</sup> behandelten Lösung der allgemeinen linearen Matrixgleichung

$$AXA_1 + BXB_1 + \dots + MXM_1 + N = 0.$$

Dagegen geben TURNBULL<sup>2)</sup> für einen besonderen Fall von  $AX + XB = C$  und BAKER<sup>3)</sup> für die Gleichung  $XAX = B$  reine Lösungen. Hierher gehört auch die „reine“ Lösung der linearen Quaternionengleichung  $\alpha \xi \beta + \gamma \xi \delta = \varepsilon$ , die schon HAMILTON<sup>4)</sup> und TAIT<sup>5)</sup> geben und die durch L. VON SCHRUTTKA<sup>6)</sup> verallgemeinert wurde.

§ 2.

Wir setzen voraus, dass in

$$AX + XB = C. \quad \dots \quad (1)$$

die Matrices  $A$  und  $B$  nicht-singulär ( $\det A \neq 0$ ,  $\det B \neq 0$ ) und dass

<sup>1)</sup> A. R. RICHARDSON, *Proceed. London Mathem. Soc.* 2, 28 (1928), p. 395—420.

<sup>2)</sup> H. W. TURNBULL, *Atti Congres Bologna* (1928), Bd. II, p. 68.

<sup>3)</sup> H. F. BAKER, *Proceed. Cambridge Phil. Soc.* 23, (1925), p. 22.

<sup>4)</sup> W. R. HAMILTON, *Elements of Quaternions* (1866), p. 410.

<sup>5)</sup> P. G. TAIT, *An elementary Treatise of Quaternions* (1867), p. 123.

<sup>6)</sup> L. VON SCHRUTTKA, *Wiener Sitzungsberichte* 115, Abt. IIa (1906), p. 739—775.  
Vgl. auch H. ROTHE, *Mathem. Enzykl.* III AB 11, p. 1335.

die zugehörigen Minimalpolynome vom  $p$ -ten resp. vom  $q$ -ten Grade sind. Dann haben wir

$$\left. \begin{aligned} A^p &= a_1 A^{p-1} + a_2 A^{p-2} + \dots + a_{p-1} A + a_p E \\ B^q &= b_1 B^{q-1} + \dots + b_{q-1} B + b_q E \end{aligned} \right\} \cdot \cdot \cdot \quad (2)$$

wobei  $E$  die Einheitsmatrix,  $a_p \neq 0, b_q \neq 0$  und die  $a_i$  bzw.  $b_k$  affine Invarianten von  $A$  resp.  $B$  sind.

Wir multiplizieren nun (1) linker Hand der Reihe nach mit  $A, A^2, \dots, A^{p-1}$ ; dies gibt  $p$  Gleichungen

$$A^k X + A^{k-1} XB = A^k C \quad (k = 1, 2, \dots, p).$$

Diese Gleichungen multiplizieren wir rechter Hand mit  $B, B^2, \dots, B^{q-1}$  und erhalten so  $p \cdot q$  Gleichungen

$$A^k XB^{m-1} + A^{k-1} XB^m = A^{k-1} CB^{m-1} \quad \left( \begin{matrix} k = 1, 2, \dots, p \\ m = 1, 2, \dots, q \end{matrix} \right) \quad (3)$$

Nach (2) ist hier jedes  $A^p XB^{m-1}$  und jedes  $A^{k-1} XB^q$  linear und homogen auszudrücken in den  $A^r XB^s$  mit  $r < p$  und  $s < q$ . Wir haben dann  $p \cdot q$  lineare Gleichungen mit ebensovielen Unbekannten

$$A^r XB^s \quad \left( \begin{matrix} r = 0, 1, 2, \dots, p-1 \\ s = 0, 1, 2, \dots, q-1 \end{matrix} \right)$$

und zwar Gleichungen mit *skalaren* Koeffizienten. Sind diese Gleichungen überhaupt lösbar (wovon man die Möglichkeit leicht durch spezielle Beispiele nachweist), so folgt, dass die gesuchte Matrix  $X$  die Form hat

$$X = \sum_{r=0}^{p-1} \sum_{s=0}^{q-1} a_{rs} A^r C B^s \quad \cdot \cdot \cdot \quad (4)$$

wo die  $a_{rs}$  rational von den Koeffizienten  $a_i$  und  $b_k$  der Gleichungen (2) abhängen.

**Mathematics.** — *Curved  $n$ -dimensional varieties containing  $n$  systems of straight lines.* By J. A. BARRAU. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of January 30, 1932).

§ 1. Imagine a species of geometrical entities  $A$  that can be indicated "smoothly", i.e. without any singularity, by homogeneous coordinates  $\{x_i\}$  eventually satisfying certain fundamental relations  $P\{x_i\} = 0$ , where the  $P$  are polynomial.

Take also a second species of entities  $B$ , not necessarily different from the first, smoothly indicated by homogeneous coordinates  $\{y_i\}$  with eventual fundamental relations  $Q\{y_i\} = 0$ .

Then the new entities obtained by the combination of an  $A$  with a  $B$  correspond smoothly to the homogeneous coordinates

$$X_{ij} = x_i y_j$$

satisfying the fundamental relations:

$$\left. \begin{aligned} P(X_{ij}) = 0, j \text{ const.}; \quad Q(X_{ij}) = 0, i \text{ const.}; \\ \left| \begin{array}{cc} X_{ij} & X_{kj} \\ X_{il} & X_{kl} \end{array} \right| = 0, i \neq k, j \neq l. \end{aligned} \right\} \dots \dots (1)$$

If the  $A$  and  $B$  belong to the same species the combination  $AB$  is evidently different from  $BA$ .

In the same way combinations  $ABC \dots$  can be smoothly indicated by coordinates

$$X_{ijk \dots} = x_i y_j z_k \dots,$$

obtained also by *multiplication of coordinates*.

Linear transformations of the  $\{x\}$ , leaving invariant the relations  $P$ , combined with linear transformations of the  $\{y\}$ , leaving the  $Q$  invariant, give rise to linear transformations of the  $\{X\}$  for which the relations (1) are invariant.

§ 2. Let  $A$  be a point  $\{x_1; x_2\}$  of a straight line, likewise  $B$  a point  $\{y_1; y_2\}$  of a line which may or may not coincide with the first, then the pair  $AB$  has the coordinates:

$$\xi_1 = X_{11} = x_1 y_1; \quad \xi_2 = X_{12} = x_1 y_2; \quad \xi_3 = X_{21} = x_2 y_1; \quad \xi_4 = X_{22} = x_2 y_2,$$

satisfying the fundamental relation:

$$\xi_1 \xi_4 - \xi_2 \xi_3 = 0 \dots \dots \dots (2)$$

Hence the pairs  $AB$  correspond smoothly to the points  $P \equiv \{\xi_1; \xi_2; \xi_3; \xi_4\}$  of the quadric surface (2); the pairs  $AB$  for which  $A$  is constant correspond to the generators of one system, the pairs  $AB$  with constant  $B$  to the generators of the other.

§ 3. The combinations  $ABC$ ,

$$A \equiv \{x_1; x_2\}, \quad B \equiv \{y_1; y_2\}, \quad C \equiv \{z_1; z_2\}$$

correspond to points:

$$P \equiv \{\xi_1; \xi_2; \xi_3; \xi_4; \xi_5; \xi_6; \xi_7; \xi_8\},$$

where

$$\begin{aligned} \xi_1 &= x_1 y_1 z_1 & \xi_2 &= x_1 y_1 z_2 & \xi_3 &= x_1 y_2 z_1 & \xi_4 &= x_1 y_2 z_2 \\ \xi_5 &= x_2 y_1 z_1 & \xi_6 &= x_2 y_1 z_2 & \xi_7 &= x_2 y_2 z_1 & \xi_8 &= x_2 y_2 z_2. \end{aligned}$$



The  $\{\xi\}$  satisfy the fundamental relations:

$$\left. \begin{aligned} \xi_1 \xi_4 - \xi_2 \xi_3 = 0 & \quad \xi_1 \xi_6 - \xi_2 \xi_5 = 0 & \quad \xi_1 \xi_7 - \xi_3 \xi_5 = 0 & \quad \xi_1 \xi_8 - \xi_4 \xi_5 = 0 \\ \xi_5 \xi_8 - \xi_6 \xi_7 = 0 & \quad \xi_3 \xi_8 - \xi_4 \xi_7 = 0 & \quad \xi_2 \xi_8 - \xi_4 \xi_6 = 0 & \quad \xi_2 \xi_7 - \xi_3 \xi_6 = 0 \end{aligned} \right\} (3)$$

The degree of freedom of  $P$ , as of  $ABC$ , is 3; hence the system of equations (3) defines a 3-dimensional variety  $V_3$  in 7-dimensional space  $S_7$ . This variety,  $\Pi$ , has no singular points and all its points  $P$  are equivalent in a projective sense. Indeed, any combination  $A_2 B_2 C_2$  can be linearly transformed into  $A_1 B_1 C_1$ , (3) remaining invariant, such a transformation arises by combining a transformation of the  $\{x\}$  transforming  $A_2$  into  $A_1$  with one of the  $\{y\}$ ,  $B_2 \rightarrow B_1$  and one of the  $\{z\}$ ,  $C_2 \rightarrow C_1$ .

The degree of  $\Pi$  is six. Indeed, combining in every possible order three points, for which may be taken without loss of generality  $\{0; 1\}$ ,  $\{1; 0\}$  and  $\{1; 1\}$ , six points  $P$  arise:

$$\begin{aligned} P_1 &\equiv \{0; 0; 1; 0; 0; 0; 1; 0\} & P_2 &\equiv \{0; 0; 0; 0; 1; 0; 1; 0\} \\ P_3 &\equiv \{0; 1; 0; 1; 0; 0; 0; 0\} & P_4 &\equiv \{0; 1; 0; 0; 0; 1; 0; 0\} \\ P_5 &\equiv \{0; 0; 0; 0; 1; 1; 0; 0\} & P_6 &\equiv \{0; 0; 1; 1; 0; 0; 0; 0\} \end{aligned}$$

These points satisfy the relation

$$P_1 + P_3 + P_5 = P_2 + P_4 + P_6,$$

so they belong to one  $S_4$ , also any point, i.e.  $P_6$ , is the only and single point of intersection of  $\Pi$  with the  $S_4$  containing the five other points  $P$ :

$$P = \lambda_1 P_1 + \lambda_2 P_2 + \lambda_3 P_3 + \lambda_4 P_4 + \lambda_5 P_5,$$

hence the degree of  $\Pi$  is  $6 \times 1 = 6$ .

Another proof will be given in § 5.

$\Pi$  contains three systems, each of  $\infty^2$  straight lines  $l$ : one system  $\alpha$ , in which  $A$  is variable,  $B$  and  $C$  are constant, e.g.

$$\{\lambda; \mu\} \quad \{c; d\} \quad \{e; f\},$$

one system  $\beta$ , e.g.

$$\{a; b\} \quad \{\lambda; \mu\} \quad \{e; f\},$$

one system  $\gamma$ , e.g.

$$\{a; b\} \quad \{c; d\} \quad \{\lambda; \mu\},$$

for in each case the  $\{\xi\}$  are linear and homogeneous functions of the parameters  $\{\lambda; \mu\}$ .

Through each point  $P$  of  $\Pi$  passes one  $l_\alpha$ , one  $l_\beta$ , one  $l_\gamma$ ; these three lines form the complete intersection of  $\Pi$  and the  $S_3$  tangent to it in  $P$ ; so there are no other straight lines on  $\Pi$  through  $P$  and as all the

points  $P$  are equivalent, there are no other lines on  $\Pi$  but the  $l_\alpha$ ,  $l_\beta$  and  $l_\gamma$ .

$\Pi$  contains three systems, each of  $\infty^1$  quadric surfaces  $H$ , one system  $\alpha$ , in which  $A$  is constant,  $B$  and  $C$  are variable, e.g.

$$\{a; b\} \quad \{\lambda; \mu\} \quad \{\nu; \kappa\},$$

one system  $\beta$ , e.g.

$$\{\lambda; \mu\} \quad \{c; d\} \quad \{\nu; \kappa\},$$

one system  $\gamma$ , e.g.

$$\{\lambda; \mu\} \quad \{\nu; \kappa\} \quad \{e; f\},$$

each  $H_\alpha$  is formed by one regulus of  $l_\beta$  and one of  $l_\gamma$ , each  $H_\beta$  by  $l_\alpha$  and  $l_\gamma$ , each  $H_\gamma$  by  $l_\alpha$  and  $l_\beta$ .

Through each point  $P$  passes one  $H_\alpha$  containing the  $l_\beta$  and the  $l_\gamma$  through  $P$ , one  $H_\beta$  containing the  $l_\alpha$  and the  $l_\gamma$ , one  $H_\gamma$  containing the  $l_\alpha$  and the  $l_\beta$ .

Each  $l_\alpha$  belongs to one  $H_\beta$ , locus of the  $\infty^1$   $l_\gamma$  intersecting the  $l_\alpha$ ; each  $l_\alpha$  belongs to one  $H_\gamma$ ; there are no  $l_\alpha$  that intersect a given  $l_\alpha$  — hence  $\Pi$  contains no quadrics, but  $H_\alpha$ ,  $H_\beta$  and  $H_\gamma$ .

Each  $l_\alpha$  has one point in common with each  $H_\alpha$ ;  
e.g. for the  $l_\alpha$ ;

$$\{ \quad \} \quad \{c; d\} \quad \{e; f\}$$

and the  $H_\alpha$ ;

$$\{a; b\} \quad \{ \quad \} \quad \{ \quad \}$$

this point is

$$\{a; b\} \quad \{c; d\} \quad \{e; f\}$$

Likewise each  $l_\beta$  has one point of intersection with each  $H_\beta$ , and each  $l_\gamma$  with each  $H_\gamma$ .

A  $l_\alpha$  has no point in common with a  $H_\beta$ , or  $H_\gamma$ , excepted when it belongs to it.

Two  $H$  of one system have no intersection; two  $H$  of different systems have a  $l$  in common, e.g. a  $H_\alpha$  and a  $H_\beta$  a  $l_\gamma$ ; three  $H$  of different systems have one point in common.

An algebraic curve on  $\Pi$ , not belonging to one  $H_\alpha$ , and of degree  $n$ , which intersects one  $H_\alpha$  in  $p$  points, intersects each  $H_\alpha$  in  $p$  points. For if we choose in the first  $H_\alpha$  a point not coinciding with one of the points of intersection, that  $H_\alpha$  belongs with the  $H_\beta$  and the  $H_\gamma$  passing through the chosen point to one  $S_6$ . This  $S_6$  intersects the given curve in the  $p$  points on  $H_\alpha$  and in  $(n-p)$  other points each of which belongs to  $H_\beta$  or to  $H_\gamma$ . Another  $H'_\alpha$  forms with the same  $H_\beta$  and  $H_\gamma$  another  $S'_6$ ; this  $S'_6$  intersects the curve in the same  $(n-p)$  points of  $H_\beta$  and  $H_\gamma$ , leaving  $n-(n-p)=p$  points of intersection with  $H'_\alpha$ .

Hence the numbers of points of intersection  $\{p; q; r\}$  with the  $H_\alpha$ ,

$H_\beta$  and  $H_\gamma$  are constant for a curve not belonging to one  $H$ ; the degree of such a curve is

$$n = p + q + r,$$

being the total number of points of intersection with a  $S_6$  as above, having with  $\Pi$  three  $H$  in common.

But if the curve belongs to a  $H$ , e.g. a  $H_\alpha$ , it has no intersection with another  $H'_\alpha$ , so  $p = 0$  is again constant and  $n = q + r$ .

An algebraic surface of degree  $N$  on  $\Pi$  that intersects one  $l_\alpha$  in  $P$  points, intersects also every other  $l_\alpha$ , which it does not contain, in  $P$  points. For if we draw through a point of  $l_\alpha$  not belonging to the surface the  $l_\beta$  and the  $l_\gamma$ , also through the pairs of these three lines the  $H_\alpha$ ,  $H_\beta$  and  $H_\gamma$ , then the curve of intersection of the surface with the  $S_6$  through the three  $H$  degenerates into a curve on  $H_\alpha$ , a curve on  $H_\beta$  and a curve on  $H_\gamma$ . The curve on  $H_\gamma$  is a  $\{P; Q\}$ -curve if  $l_\beta$  is intersected in  $Q$  points, that on  $H_\beta$  is a  $\{P; R\}$ -curve, if  $l_\gamma$  is intersected in  $R$  points, that on  $H_\alpha$  is a  $\{Q; R\}$ -curve and

$$N = (P + Q) + (P + R) + (Q + R) = 2(P + Q + R).$$

Any other  $l'_\alpha$  intersects  $H_\alpha$  in one point, the  $l'_\beta$  and the  $l'_\gamma$  through this point belong to  $H_\alpha$  and intersect resp. in  $Q$  and  $R$  points. If  $P'$  is the number of points of intersection with  $l'_\alpha$ , then again  $N = 2(P' + Q + R)$ , hence  $P' = P$ .

Another proof of the invariance of  $\{p; q; r\}$  and  $\{P; Q; R\}$  will be given in § 4.

§ 4.  $\Pi$  is rational, i.e. it may be brought to correspond birationally to ordinary projective space  $S_3$ . To prove this we choose in  $S_3$  three pencils of planes with axis **a**, **b**, **c** in general position, the point  $\{a; b\} \{c; d\} \{e; f\}$  of  $\Pi$  is made to correspond to the point of intersection of the three planes having in the pencils **a**, **b**, **c** resp. the homogeneous coordinates  $\{a; b\}$ ,  $\{c; d\}$ ,  $\{e; f\}$ .

The lines  $l_\alpha$ ,  $l_\beta$ ,  $l_\gamma$  correspond — safe singular cases treated hereafter — to transversals over **b** and **c**, **a** and **c**, **a** and **b**; the  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$  correspond to planes through **a**, **b**, **c**.

The singularities of the correspondance are:

to a transversal  $t$  over **a**, **b**, **c** corresponds a single point  $S$ , to the quadric surface  $T$  through **a**, **b**, **c** a curve  $\sigma$ , locus of points  $S$ ;

to a point of **a** corresponds a line  $l_\alpha$  that intersects  $\sigma$ , to **a** the scroll  $\Sigma_\alpha$  of  $l_\alpha$ , to **b** the scroll of  $l_\beta$ , to **c** the scroll of  $l_\gamma$  intersecting  $\sigma$ .

To a curve of degree  $n$  in  $S_3$  having  $p$  points of intersection with **a**,  $q$  with **b**,  $r$  with **c**, corresponds a curve on  $\Pi$  for which

$$p = n - p, \quad q = n - q, \quad r = n - r, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$n = 3n - (p + q + r); \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(4) gives another proof of the invariance of  $\{p; q; r\}$ .

Two curves  $\{p; q; r\}$  need not belong to the same species, this not being the case with the curves in  $S_3$  to which they correspond.

To a surface of degree  $n$  in  $S_3$ , for which  $a$  is  $p$ -fold,  $b$  is  $q$ -fold,  $c$  is  $r$ -fold, corresponds a surface on  $\Pi$  for which

$$P = n - q - r, \quad Q = n - p - r, \quad R = n - p - q, \quad \dots \quad (6)$$

and

$$N = 2(P + Q + R) = 6n - 4(p + q + r); \quad \dots \quad (7)$$

(6) gives another proof of the invariance of  $\{P; Q; R\}$ .

The surfaces  $\{P; Q; R\}$  belong to one species.

A generator of  $T$  belonging to the same set as  $a, b, c$  has one point in common with every transversal  $t$ , such a generator corresponds to  $\sigma$ , hence  $\sigma$  is a cubic  $\sigma^3$ .

All the curves  $\{1; 1; 1\}$  still form one single species, hence the degree of a scroll  $\Sigma$  is the same as that of any other scroll the generators of which are lines  $l$ , e.g.  $l_\alpha$ , intersecting a  $\{1; 1; 1\}$ -curve. To such a surface corresponds a quadric surface in  $S_3$ , containing  $b$  and  $c$ , so  $n = 2$ ,  $p = 0$ ,  $q = 1$ ,  $r = 1$  and  $N = 12 - 8 = 4$ , hence the  $\Sigma$  are  $\Sigma^4$ .

To a  $\{p; q; r\}$ -curve on  $\Pi$  having  $s$  points of intersection with the singular curve  $\sigma^3$ , corresponds a curve in  $S^3$  for which

$$\left. \begin{aligned} n &= p + q + r - s \\ p &= \quad q + r - s \\ q &= p \quad + r - s \\ r &= p + q \quad - s \end{aligned} \right\} \dots \dots \dots (8)$$

For  $s = 0$  the curve on  $\Pi$  is general, i.e. free from  $\sigma$ .

In  $S_3$  this means that the  $2n = 2(p + q + r)$  points of intersection of the corresponding curve with  $T$  are distributed on  $a, b, c$  resp. to the numbers of  $q + r, p + r, p + q$ , there are no other intersections with  $T$ .

If  $p \cong q \cong r$  then  $q + r$  is the highest possible value of  $s$ , if this value is attained for  $p = q = r$  the corresponding curve in  $S_3$  is general, i.e. free from  $a, b, c$ .

To a surface  $\{P; Q; R\}$  on  $\Pi$  of degree  $N = 2(P + Q + R)$  and containing  $\sigma^3$  with a multiplicity  $S$  corresponds a surface in  $S_3$  for which

$$\left. \begin{aligned} n &= P + Q + R - 2S \\ p &= P - S, \quad q = Q - S, \quad r = R - S. \end{aligned} \right\} \dots \dots \dots (9)$$

If  $S = 0$  the surface on  $\Pi$  is general, i.e. free from  $\sigma$  and the corresponding surface intersects  $T$  exclusively along transversals  $t$  corresponding to the points of intersection of the surface on  $\Pi$  and  $\sigma$ .

If  $P \cong Q \cong R$  then  $R$  is the highest possible value of  $S$ , if this value is attained for  $P = Q = R$  the corresponding surface in  $S_3$  is general, i.e. free from  $a, b, c$ .

If  $P=0$  (or  $Q=0, R=0$ ) the surface is a scroll whose generators are  $l_\alpha$  (or  $l_\beta, l_\gamma$ ).

§ 5. The number of points of intersection of *three* general surfaces

$$\{P_1; Q_1; R_1\} \quad \{P_2; Q_2; R_2\} \quad \{P_3; Q_3; R_3\}$$

on  $\Pi$ , having no curve in common, is

$$i = \begin{vmatrix} \overline{P_1} & \overline{Q_1} & \overline{R_1} \\ P_2 & Q_2 & R_2 \\ \overline{P_3} & \overline{Q_3} & \overline{R_3} \end{vmatrix} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (10)$$

a polynomium analogous to a determinant with the difference that its terms are not given alternately the signs  $+$  and  $-$ , but permanently the sign  $+$ .

So

$$i = P_1 Q_2 R_3 + P_1 Q_3 R_2 + P_2 Q_1 R_3 + P_2 Q_3 R_1 + P_3 Q_1 R_2 + P_3 Q_2 R_1.$$

Indeed the surfaces  $\{P; Q; R\}$  in general position correspond to a linear system of surfaces in  $S_3$  and the number of points of intersection of three of these follows the principle of continuity, the number is constant if finite. So each corresponding surface may be replaced by  $P$  planes through  $a$ ;  $Q$  through  $b$ ,  $R$  through  $c$ ; hence (10).

The number of points of intersection diminishes if the three surfaces contain the same curve, this is always the case if their position is not general (for then they contain  $\sigma$ ) — in each case the true number can be found in  $S_3$ .

For three surfaces  $\{1; 1; 1\}$ :

$$\begin{vmatrix} \overline{1} & \overline{1} & \overline{1} \\ 1 & 1 & 1 \\ \overline{1} & \overline{1} & \overline{1} \end{vmatrix} = 1 \cdot 1 \cdot 1 = 3! = 6.$$

But such a surface  $\{1; 1; 1\}$  is the complete intersection of  $\Pi$  and a linear  $S_6$ :

$$A_1 \xi_1 + A_2 \xi_2 + A_3 \xi_3 + A_4 \xi_4 + A_5 \xi_5 + A_6 \xi_6 + A_7 \xi_7 + A_8 \xi_8 = 0,$$

hence  $i=6$  is the number of points of intersection of  $\Pi$  and the linear  $S_4$  common to three  $S_6$ , which gives another proof of the degree of  $\Pi$ .

The number of points of intersection for a  $\{p; q; r\}$ -curve and a  $\{P; Q; R\}$ -surface is, if it is finite,

$$i = pP + qQ + rR. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11)$$



The curve of intersection of two general surfaces  $\{P_1; Q_1; R_1\}$ ,  $\{P_2; Q_2; R_2\}$  is a  $\frac{\overline{P_1 Q_1 R_1}}{\overline{P_2 Q_2 R_2}}$ -curve, or

$$p = \frac{\overline{Q_1 R_1}}{\overline{Q_2 R_2}}, q = \frac{\overline{P_1 R_1}}{\overline{P_2 R_2}}, r = \frac{\overline{P_1 Q_1}}{\overline{P_2 Q_2}} \} \dots \dots \dots (12)$$

For

$$p = \frac{\overline{1 \ 0 \ 0}}{\overline{P_2 \ Q_2 \ R_2}}, q = \frac{\overline{0 \ 1 \ 0}}{\overline{P_2 \ Q_2 \ R_2}}, r = \frac{\overline{0 \ 0 \ 1}}{\overline{P_2 \ Q_2 \ R_2}}.$$

§ 6.  $\Pi$  is in smooth correspondance to the lineo-linear congruence of planes in  $S_5$  having one point in common with each of three straight lines  $a, b, c$  in general position — there is one plane in the congruence through each point not on  $a, b$  or  $c$  and one plane in each  $S_4$  not containing  $a, b$  or  $c$ . To fix the correspondance we have only to consider the points  $A, B, C$  in which the plane in  $S_5$  intersects  $a, b, c$  as the points  $A, B, C$  of § 3.

A line  $l$  of  $\Pi$  corresponds to a set of planes  $ABC$  in which two of the points are kept constant; a  $H$  of  $\Pi$  corresponds to a set of planes  $ABC$  where one of the points is constant.

Curves  $\{p; q; r\}$  and surfaces  $\{P; Q; R\}$  correspond to sets of planes  $ABC$  obeying the formulas (10), (11) and (12).

§ 7. The pairs of points,  $n=2$  (§ 2) and the triplets,  $n=3$  (§ 3—§ 6) are the first of a series of cases, which consider sets of  $n$  points belonging to  $n$  straight lines, one point on each line.

These sets correspond, for any  $n$ , to the points of an  $n$ -dimensional variety  $V_n^{n!}$  of degree  $n!$  in a linear space  $S_{2^n-1}$  of  $2^n-1$  dimensions.

This variety  $\Pi_n$  contains  $n$  systems of lines  $\Pi_1, \binom{n}{2}$  systems of  $\Pi_2, \dots, \binom{n}{k}$  systems of  $\Pi_k, \dots, \binom{n}{n-1} = n$  systems of  $\Pi_{n-1}$ .

Curves on  $\Pi_n$  have indices  $\{p_1 \dots p_n\}$  where the  $p$  are the numbers of points of intersection with the  $\Pi_{n-1}$  of the various systems; the  $V_{n-1}$  of  $\Pi_n$  have indices  $\{P_1 \dots P_n\}$  where the  $P$  are the numbers of points of intersection with the lines  $\Pi_1$  of the various systems.

The number of points of intersection of  $n$  varieties  $V_{n-1}$  is in the general case

$$i = \frac{P_{11} \dots P_{n1}}{P_{1n} \dots P_{nn}}$$



temperate zones, for the same altitude of the sun, which fact he contributes to the lense shape of the atmosphere<sup>1)</sup>.

Dr. D. MULDER, physician at Bandoeng is, on medical grounds, of the opinion, that the proportion of ultraviolet in the Indian sunlight can certainly not be very small, and he thinks that photographic observations do not disagree with this<sup>2)</sup>.

For this reason it seemed important to determine by accurate measures extending over an appreciable time the strength of the ultraviolet in Bandoeng, for direct sunlight as well as for diffuse light. These observations were for some time accompanied by determinations of the photographic light with the neutral wedge photometer ("Graukeilphotometer").

On account of our unforeseen departure to Europe, these determinations had to be brought to a close in August 1929, and though the time is certainly insufficient for accurate data, these observations extending, apart from certain gaps, over a whole year, are not without importance as a contribution in this unexplored domain.

Bandoeng is situated on  $107.5^{\circ}$  eastern longitude and  $6^{\circ} 57'$  southern latitude. The observations took place on the very spacious square surrounded by the buildings of the physical laboratory of the Technische Hoogeschool 760 meters above sea level. The laboratory is a long building of only one storey. For the purpose of observing the ultraviolet a 10 meter high iron tower was erected, so that the entire horizon was free. The nearest mountains were the Prahoe and the Boerangrang, which, having an altitude of about 1300 meters above Bandoeng at a distance of 17 K. M., hardly intercepted the light of the sky, so that the radiation came unobstructed from practically the entire upper hemisphere, which is of great importance for observations of the diffuse light. The more so, since the ground uviol-glass used for determining the illumination of the horizontal plane by the diffuse sky light, diffuses very imperfectly, and for an angle of incidence of about  $80^{\circ}$  the cell receives much less than would be expected according to LAMBERT'S law. This point will be taken up when discussing the determination of the diffuse sky light.

#### *Method of observation.*

The method making use of the Cadmium cell by means of electrometric discharge was decided upon. The apparatus was a photoelectric photometer after ELSTER and GEITEL, in the special form given to it by GÜNTHER and TEGETMEYER after indications by DORNO.

The Cadmium cell, connected with a single fibre electrometer, was charged up every time by means of a Zamboni pile to a little over 120 volt,

<sup>1)</sup> C. DORNO, Die ultravioletten Sonnen- und Himmelsstrahlung in tropischen Gegenden, Die Naturw., 18e Jahrg., Heft 12.

<sup>2)</sup> Dr. D. MULDER, Handelingen van het vierde Nederl.-Ind. Natuurwetenschappelijk Congres 1926, pag. 148.

and the time determined in which the incident sunlight produced a discharge from 120 to 90 volt. In this region the sensitivity curve of the cell is linear, and the same thing is the case for the calibration curve of the electrometer. The latter was repeatedly verified during the research by calibrating the electrometer.

By inserting various diaphragms, the time of discharge was kept within not too wide limits. For very small intensities, discharge took place over a smaller range of potential, taking care that always the time of discharge for the smaller interval was accurately compared with the time observed for the usual drop from 120 to 90 volt. The ratio of the diaphragms was also carefully determined by experiments on the apparatus itself.

Special care was taken to keep cells as well as electrometer dry. This is absolutely necessary in the tropics, and greatly hampers the work with electrometers. Because of the construction of the cells, the chemicals for drying had to be removed during observations, to which there is no objection, since the measurements took place in the sunshine. When not in use, cells and electrometer had to be provided with good drying materials, and moreover the whole apparatus was then enclosed in an electrically heated box, so that the temperature was always above the surrounding. On every observing day, the leakage was repeatedly determined, and, if necessary, allowed for. However, it remained within the limit of observational error in nearly all cases.

In the above mentioned way it was possible to reduce the time of discharge to always the same fall of potential of 120 to 90 volts and the same diaphragm, with an uncertainty of only a few percent.

The intensity was computed according to the formula

$$I = \frac{10000}{t} \log \frac{120}{90} = \frac{1250}{t}$$

where  $t$  is expressed in seconds.

## § 2. *Reduction of the cells to the standard.*

The Cadmium cell method has, as is well known, the great advantage of simplicity in treatment and of inexpensive and easily movable apparatus. The main disadvantage is, that the Cadmium cell does not measure the ultraviolet intensity, but rather the integral of the intensity of each spectral element multiplied by the corresponding sensitivity of the cell. The Cadmium cell only responds to ultraviolet rays, and seems, up to about 3200 Angstrom, to be very little sensitive. The sensitivity rises very rapidly for shorter wavelengths, and has a maximum for a wavelength, which is not the same for different cells. For the two cells for which HAUSSER, at DORNO's<sup>1)</sup> request, determined the sensitivity curve, the maximum is situated at 2800 and at 2650 Angstrom, therefore in both

<sup>1)</sup> C. DORNO, Meteor. Zeitschr., Sept. 1924, pag. 245.



cases outside the spectral region of solar radiation. For both cells the sensitivity at 2900 Å is about six times that at 3100 Å. The integrated intensity, which is measured, has therefore only relative value, and measures with different cells can only be compared, if the sensitivity of the two cells has been compared for as many solar altitudes, that is as many spectral regions, as possible.

The cell Cd II of DORNO and his collaborators, which is used by them for many years, is generally adopted as a standard. Our observations have been reduced to this cell, and correspond therefore to the Davos scale.

A great difficulty, however, is, that the sensitivity curve of our two cells 5450 and 5480 of GÜNTHER and TEGETMEYER deviates very appreciably from the one of Cd II. This seems to be the case for the majority of newer cells. It follows from the fact that the sensitivity ratio of our cells to Cd II strongly depends on the solar altitude. Before we took the cells to India, they were in February 1928 compared with the Davos cell for solar altitudes up to  $35^\circ$ . The very pronounced dependance of the reduction factor on the sun's altitude made us hesitate to extrapolate the calibration to higher altitudes, as would be necessary, since we worked with solar altitudes up to  $90^\circ$ . Therefore publication was delayed, until recalibration had taken place in Davos for the maximum solar altitude.

At first, calibrations at various times of the year, did not agree satisfactorily, if observations at the same solar altitude were compared. Dr. MÖRIKOFER and Dr. LEVY, Director and collaborator of the Physical-Meteorological Observatory in Davos, have taken great pains in thoroughly investigating this matter. Theoretical considerations made them express the sensitivity ratio, not as a function of solar altitude, but as a function of the *minos* ratio. This is defined as the intensity ratio of unfiltered and filtered sunlight as directly given by the Cadmium cell, the filter being *minos* glas, which kind of glass lets through rays down to 3130 Å, the latter part however much weakened.

Reduction factors determined in this way agree well, even for different seasons. It is to be regretted, that the calibrations of 1928 cannot be arranged according to *minos* ratios, since at that time only unfiltered observations were taken. Fig. 1 gives the various calibrations, arranged according to solar altitudes, Fig. 2 the same, arranged according to *minos* ratios. Both figures were kindly put at my disposal by Dr. LEVY.

Dr. LEVY further derived, that in general reduction factor  $E$  and *minos* ratio  $Q$  are in first approximation related by  $EQ^a = \text{constant}$ , where  $a$  is a constant.

This first approximation consists in the assumption, that the Cadmium cell enables us to measure the intensity of a definite wavelength in a relative measure, in other words, that the effective wavelength is independent of solar altitude. The same thing is assumed for the cell with filter, in which case the effective wavelength is larger and the relative measure a different one.



Though this condition, either with or without filter, is certainly not fulfilled for our cell 5450, with which our measurements took place, the

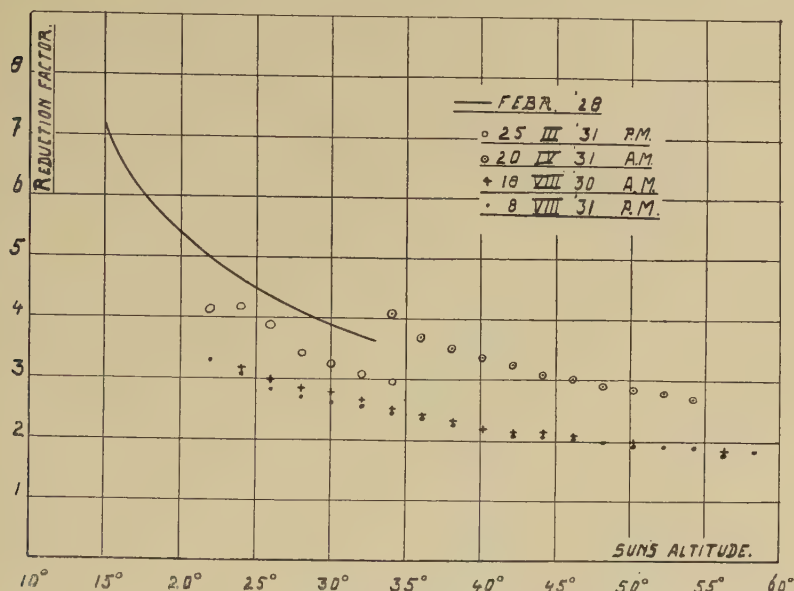


Fig. 1. Calibrations of the cell 5450, arranged according to solar altitudes.

results of the calibration agree rather well with the formula  $EQ^a = \text{constant}$ , and we find with  $a=1$  a maximum deviation of about 5%. It is true that for very small minos values the deviations are somewhat larger, but for Davos the observations have little accuracy in this region, and in Bandoeng they are still less accurate, for which reason very few observations were taken at these small minos values.

In Fig. 2, the line representing the means of the reduction factors as well as the line  $EQ = \text{constant}$  is drawn. From the fact that these two lines nearly coincide follows therefore, that our cell with minos filter has about the same effective wavelength as the Davos cell CII without minos.

Our observations in Bandoeng, which always were accompanied by filtered observations, indicate minos ratios of 4 to 15. Comparisons with the cell CdII only took place up to the minos ratio 10. Extrapolation over a fairly large region is therefore necessary. Because of the rather good agreement of the reduction factors with the line  $EQ = \text{constant}$ , we could assume that this line gives the correct values and thus extrapolate. At the same time this would give the advantage of a simple reduction to the Davos scale. We simply would have to multiply our filtered observations by a constant factor.

Another way of extrapolating is, that we prolong the line representing the means of the reductions, and thus extrapolate graphically. In the present case we have chosen the latter procedure, because the experimental calibration curve, just at  $Q=10$  has the tendency of rising a little

above the line  $EQ = \text{constant}$ , so that the deviations of the latter line from the real values become perhaps somewhat larger than in the region

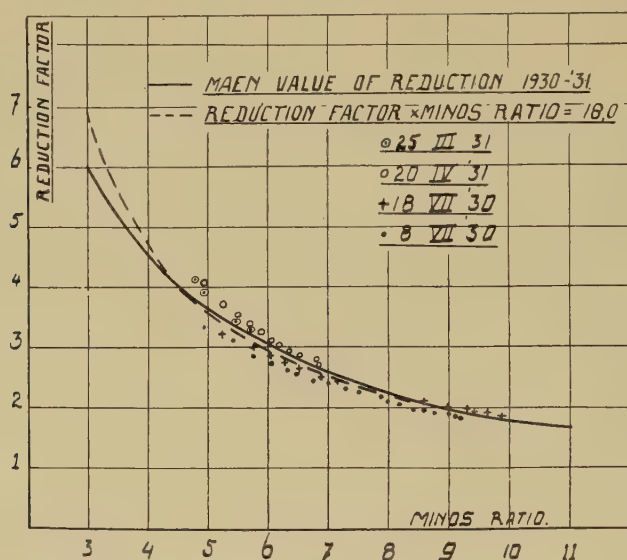


Fig. 2. Calibrations of the cell 5450, arranged according to minos ratios.

up to  $Q = 10$ . The advantage of simple calculations was not applicable to us, since computations had already been completed by means of graphical extrapolation, when Dr. LEVY's considerations came to our knowledge. An uncertainty remains in any case for the reduction factors at minos ratios above 10, which could only be removed by calibration with the standard cell up to about  $85^\circ$  solar altitude, which is practically impossible.

Since the reduction factor for our cell is diminishing to one third of its value for minos ratios from 4 to 15, reduction to the Davos scale for a cell as ours is only possible if calibrations are done with extreme care, and only for observations accompanied by determinations with filter.

In conclusion we remark, that we never experienced any fatigue in our cells.

### § 3. Results of observations of ultraviolet solar intensity.

These are given in Tables I and II, in Table I arranged according to the sun's altitude, in Table II according to the hours of the day, both reduced to the Davos galvanometer scale (unit  $3.5 \cdot 10^{-11}$  Amp.).

Observations were carried out exclusively in the morning and the early afternoon. No measurements were ever taken after 2 p.m. Observations rarely begin at a solar altitude below  $20^\circ$ . On account of the small intensity and its rapid change the observations for lower solar altitudes have little accuracy. For the same reason the minos ratio for these low

TABLE I.  
Ultraviolet intensity and Suns altitude.

Altitude	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	65°	70°	75°	80°	85°	90°
Month																
September 1928 . (3)				84	103	135	164	192	220	245	270	294	310	327		
October . . . . . (5)			67	99	129	159	191	217	245	269	292	310	327	333	340	346
January 1929 . . . (9)	7.5	22	55	97	136	161	196	233	263	294	326	353	375			
February . . . . . (6)		37	77	108	139	170	200	222	252	284	314	342	364	384	394	
March . . . . . (3)				114	157	195	223	247	268	291	314	333	352	366	379	
April . . . . . (3)			42	79	134	174	202	231	258	280	299					
May . . . . . (1)			47	77	114	154	191	224	252	278	301					
June . . . . . (4)	9.6	25	56	85	120	155	180	206	229	245						
July . . . . . (4)		39	67	98	134	166	200	235	262	292						
August . . . . . (3)				95	131	166	203	239	267	299	326	355				

altitudes can only be imperfectly determined. Since in Bandoeng the sun rises almost perpendicularly, these difficulties are greater there than in more temperate regions, where the altitude of the sun changes less rapidly.

The observations cover an entire year, the first observing day being 23<sup>d</sup> Aug. '28 the last 17<sup>th</sup> Aug. '29. The observations for these two days are in such good agreement, that a change in sensitivity of the cell in the course of the observing year becomes improbable.

Expecting nearer data from Davos, under more on the reduction factor, and not thinking that our observations should be discontinued so soon on account of our departure from India, no observations were done during November and December. The number of observing days for every month is added in parentheses. Mostly this is not very large, in certain months observations could only be done on very few days. These are the months when it rains in the morning and clouds usually begin to gather at nine. Frequently observations had to be discontinued for this reason. Perfectly cloudless days do not occur, practically, there are always clouds near the horizon, often also small white clouds in spots. Some of the

TABLE II.  
Ultraviolet intensity and time of the day,

Time of the day	7h	8h	9h	10h	11h	12h
Month						
September 1928 .		80	158	240	299	327
October.....		99	191	270	327	346
January 1929 ...	10	99	193	281	352	382
February.....	15	110	200	284	362	394
March.....		114	223	291	348	379
April.....		64	188	263	310	340
May.....		50	146	230	278	296
June.....		50	134	195	230	245
July.....		67	154	228	280	302
August.....		74	174	261	320	350

observing days were left out afterwards, since the results were clearly too small, which in those cases was confirmed by an abnormally high intensity of the diffuse light. When a few clear, almost cloudless observing days occur in the same month, their agreement is striking, e.g. for February. A little before noon, often a certain haziness occurs, by which the solar intensity diminishes somewhat. In the afternoon there usually are clouds, often showers, and, also for other reasons, this time of the day usually is less suited for observations than the morning.

A pronounced annual period at a given solar altitude does not appear from the observations. It might seem that September and June are lowest, but the differences are at any rate much less than at higher latitudes.

This shows especially if means over three months intervals are taken. These are plotted in Fig. 3 as a function of solar altitude, however it should be remarked, that the quarter of November, December and January contains only observations in January for the reason stated. The half year from May till October has a somewhat lower mean than the other half year, the difference however amounting to only 7 %. We may therefore

conclude that for the same solar altitude the ultraviolet radiation at Bandoeng shows a much smaller annual variation than e.g. at Davos.

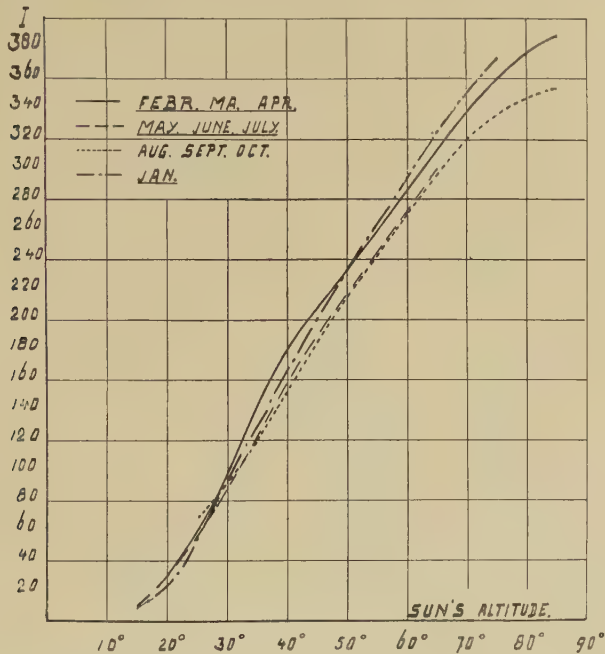


Fig. 3. Ultraviolet solar intensities, arranged according to solar altitudes.

Comparing the monthly means, arranged according to hours of the day, the differences throughout the year are of course larger, but at noon the minimum value, occurring in June, is still 62 % of the maximum value, occurring in February.

For January, March, June and September the dependance on the hour of the day is represented in Fig. 4.

For comparison of the strength of the ultraviolet in Bandoeng with temperate regions, Davos is obviously most suited, since for this location very accurate data taken with cell Cd II and extending over a long time are available. However the difference in altitude between the two locations comes in as an unknown factor. We have no accurate data on the dependance of the ultraviolet radiation on geographical elevation, and those we have diverge. We have therefore made a comparison between Arosa (1860 M.), Davos (1560 M.), Bandoeng (760 M.) and Chur (590 M.). For Arosa GÖTZ<sup>1)</sup> has collected accurate data. From these we have computed, by means of the ratio Arosa to Chur, as given on p. 48 of the paper mentioned under 1), the annual mean for Chur, and have drawn in Fig. 5 the four annual means, arranged according to solar altitude. Comparison of these four curves shows, that, at a given solar altitude,

1) Dr. F. PAUL GÖTZ, Das Strahlungsklima von Arosa, pag. 47.



Bandoeng's ultraviolet intensity, averaged over the year is less above that of Chur than corresponds to the difference in elevation. Some values for

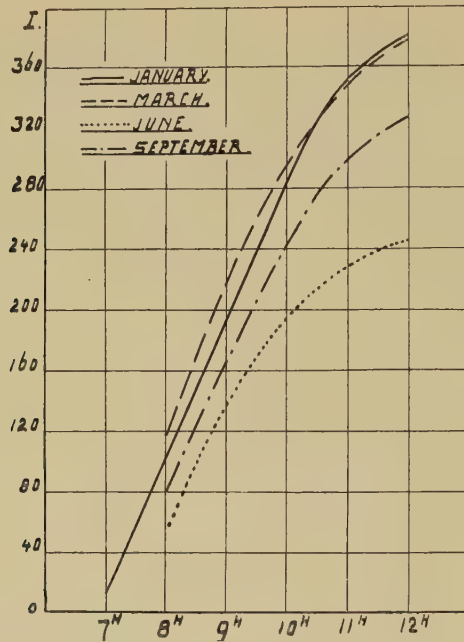


Fig. 4. Ultraviolet solar intensities arranged according to hours of the day.

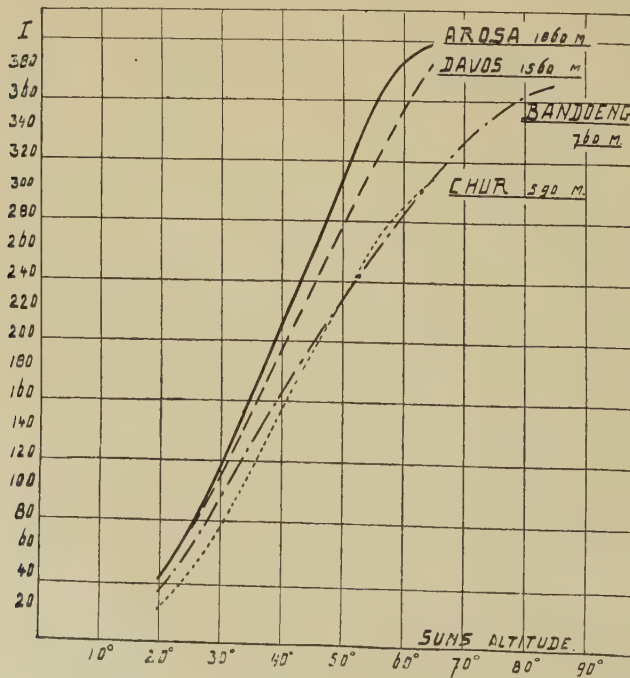


Fig. 5. Annual means of ultraviolet solar intensity for Arosa, Davos, Bandoeng and Chur.

Chur are even a little above those for Bandoeng. One might conclude from this, that the value for Bandoeng would turn out somewhat lower than for a place in Switzerland at the same elevation. The differences, however are only a few percent and the insufficient material for Bandoeng makes this conclusion uncertain; the accuracy of our observations certainly does not reach beyond a few percent. At any rate it seems that the annual mean for Bandoeng does not appreciably deviate from that of a place of observation in Switzerland at the same elevation and for the same solar altitude. We shall return to this in the next paragraph<sup>1)</sup>.

If we take the total sum of light over a year, Bandoeng even fairly exceeds Davos, which is easily understood on account of the much higher solar altitude. We shall return to this when discussing the strength of the diffuse ultraviolet.

We have refrained from giving separately the intensity of the long wave ultraviolet, which minus glass transmits, since, in our opinion, this has little value. In this matter we are entirely in accord with a consideration by Dr. LEVY in a paper on his experiences in calibrating Cadmium cells, which is to appear shortly in the "Meteorologische Zeitschrift", and of which he kindly sent us a copy. That our cell, also when used with filter, has no constant effective wavelength, follows moreover from the fact, that the effective wavelength of our cell with filter is equal to that of cell CdII without filter, as resulted from the calibrations. And of the latter the effective wavelength certainly is not constant. This greatly lessens the value of filtered observations with our apparatus as a means of determining intensities uninfluenced by extension of the spectrum into the shorter wavelengths. The glass introduced by GÖTZ as a filter which cuts off at larger wavelengths, was better in this respect.

Though our filtered observations are not of much value as intensity determinations, they are of much importance for the determination of the reduction factor, and, besides, they make it possible to carry out an estimate of the thickness of the ozone layer, with which the following paragraph deals.

Transmission coefficients were determined for the unfiltered light after reduction to the Davos scale. The values obtained are very large: for January till March on the average 0.53, for June and July 0.52, for Aug. till Oct. 0.54.

### *The thickness of the Ozone layer.*

§ 4. In order to obtain information on the thickness of the ozone layer,

<sup>1)</sup> At the time when our cell had only been compared with CdII up to 35° solar altitude, and we could not yet foresee, that the reduction factor would diminish to such an extent as afterwards turned out to be the case, our observations seemed to point out that the ultraviolet intensity of sunlight in Bandoeng exceeded even that of Davos for the same solar altitude. We made a statement to that effect in a communication before the Natuurwetenschappelijke Vereeniging in Bandoeng, however making a reserve in case the calibration might yield different results.

we have followed the method indicated by GÖTZ<sup>1)</sup>). We may assume that the intensity ratio of unfiltered to filtered radiation as given by the Cadmium cell, that is the minus ratio, is a continuous function of the length of the path in the ozone. Without entering into the nature of this function, we may say that, if, for two different measures with the same apparatus, the minus ratio is the same, then the length of the path in the ozone is also the same. The latter, in its turn, is related in a simple manner to the sun's altitude and the thickness of the ozone layer, and thus we may determine the ratio of the thickness of the ozone layer for two observations having the same minus ratios.

By this simple method we may determine.

A. The ratio of the thicknesses of the ozone layer for various periods in Bandoeng.

B. The ratio of the thickness of the ozone layer in Bandoeng and Davos at corresponding times of the year, making use of observations with our apparatus in Davos by Dr. LEVY. From the mean ozone values which are known for Davos, we may therefore make an estimate of the thickness of the ozone layer at Bandoeng.

Of course the accuracy of this method cannot come anywhere near that of the ultraviolet spectrograph of DOBSON, but nevertheless it gives a certain estimate which may provide a useful contribution on the thickness of the ozone layer in the tropics and its variation throughout the year.

As regards A, we have plotted in Fig. 6 the four means of the minus

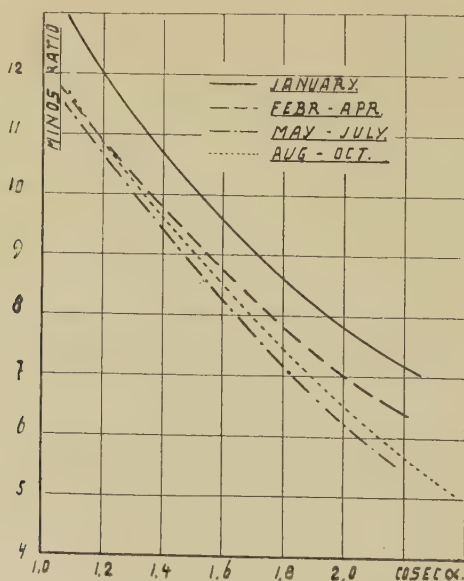


Fig. 6. Means of the minus ratio for three months intervals as functions of the cosec. of the sun's altitude.

1) Dr. F. PAUL GÖTZ, Das Strahlungsklima van Arosa, pag. 56.

ratio for three months intervals as functions of the cosec. of the sun's altitude ( $\alpha$ ). If we find that the minos ratio at  $\alpha$ , for the one curve corresponds to that of  $\alpha_2$  for the other, then we must have  $d_1 \text{ cosec. } \alpha_1 = d_2 \text{ cosec. } \alpha_2$  ( $d$  is the thickness of the ozone layer).

For the thickness of the ozone layer expressed in that for May to June as a unit, we find from August to October at minos ratios 7, 8, 9, 10, 11, the thicknesses 0,98, 0,97, 0,97, 0,97, 0,97, mean 0,97. For January (Nov. and Dec. are left out), we find in the same way 0,82, 0,85, 0,87, 0,86, 0,85, mean 0,85, for Febr. to April resp. 0,93, 0,94, 0,95, 0,95, 0,97, mean 0,95.

These observations point therefore, in agreement with DOBSON's<sup>1)</sup> results to a small variation of the thickness of the ozone layer throughout the year and fit in rather well between the observations at 10° northern and 22° southern latitude.

B. From Davos we obtained means of minos ratios from January to May and from August to October taken there with our cell and minos glass. For the sake of comparison we have also taken means of Bandoeng observations for the same intervals. Only for part of the minos ratios comparisons of the ozone layer can be made, since the large minos ratios do not occur in Davos, and the small ratios in Bandoeng have little accuracy, whereas moreover minos ratios in Bandoeng are higher than in Davos for the same solar altitudes.

Comparing the curves of January to May for Davos and for Bandoeng, we conclude that for each of the minos ratios 5, 6 and 7 the ozone layer in Bandoeng is 68 % of that in Davos.

Comparison of the curves for August to October gives for minos ratios 8, 9 and 10, an ozone layer at Bandoeng which is 94 %, 91 % and 90 % of that in Davos, average 92 %.

If we take for the mean thickness of the ozone layer in Davos the value determined by GÖTZ in Arosa<sup>1)</sup> we find as mean for January to May 3.33 m.M. and for August to October 2.79 m.M. For Bandoeng these two values become therefore 2.26 and 2.57 m.M. Taking into account the inaccuracy of our method, these values also agree rather well with those published by DOBSON<sup>1)</sup>.

Indeed, in spring the ozone layer in Davos turn out to be appreciably thicker than in Bandoeng, in the autumn the difference is not large.

In Fig. 7 the annual mean of the ultraviolet intensity for Bandoeng and the September mean for Chur are drawn, arranged according to solar altitudes (derived in the same way as described above). By this procedure periods of approximately the same thickness of ozone are compared. The month of September was chosen for Chur, because this month being in the period of thinner ozone layer, yet has rather large solar altitudes. In this case the line for Chur runs appreciably higher than that of Bandoeng. We may conclude that in periods of about equal ozone layer,

<sup>1)</sup> Dr. G. M. B. DOBSON, Nature, May 2, 1931, pag. 668.

Bandoeng has, for a given sun's altitude, somewhat less ultraviolet than exists in Switzerland at the same elevation. Perhaps this may be explained by the lenze shape of the atmosphere, as DORNO supposes.

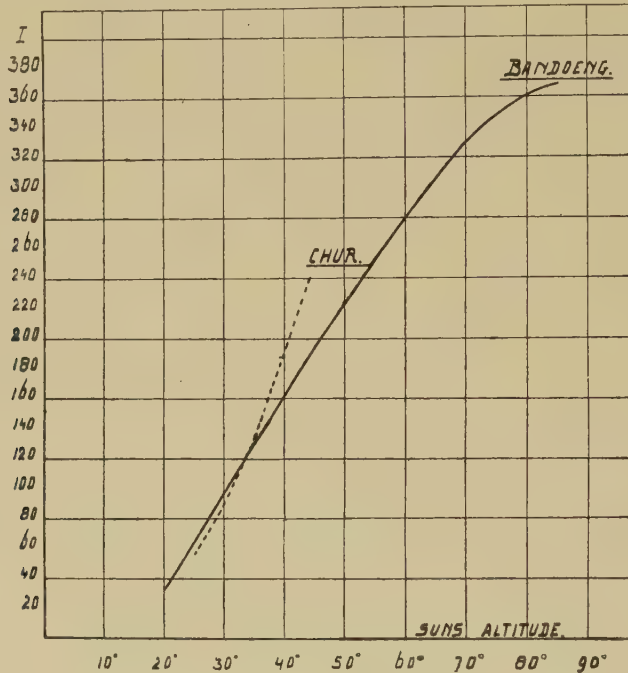


Fig. 7. Annual mean of the ultraviolet solar intensity for Bandoeng and the September mean to Chur, arranged according to solar altitude.

In conclusion we wish to express our very sincere thanks to Professor DORNO for his generous help and advice, and to Dr. MÖRIKOFER and Dr. LEVY for the great pains they have taken for the calibration of our cells.

Physics. — *On the ZEEMAN-effect in the arc spectrum of Nickel.*  
By C. J. BAKKER. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of January 30, 1932.)

§ 1. *Introduction.* In his important paper on the extension of the analysis of the Nickel arc spectrum H. N. RUSSELL<sup>1)</sup> remarks in his conclusions, that the ZEEMAN effect in this spectrum offers an extensive field of work; it may be anticipated that many *g*-values will be abnormal, especially for the higher terms, but this should be important in studying the changes of coupling of the vectors which are involved.

<sup>1)</sup> H. N. RUSSELL, Phys. Rev. 34, 821, 1929.



The present paper records the ZEEMAN effect of lines in the Nickel arc spectrum, classified mostly as combinations of the lower terms in the energy scheme. It will appear that even among those terms anomalous  $g$ -values occur, obeying PAULI's well known  $g$ -sum rule.

§ 2. *On the term scheme of Ni. I.* Though more than one thousand spectral lines belonging to the Nickel arc spectrum are known, indicating its high complexity, it has been shown by the spectroscopists, who successively have worked on the analysis of this spectrum, that the structure is regular in so far that every observed term fits into the scheme predicted by HUND's theory<sup>1)</sup>.

Nickel has the atomic number 28, corresponding to the 28 electrons surrounding the Nickel nucleus. 18 of those 28 electrons form together a so-called Argon core, consisting of the completed shells 1s, 2s, 2p, 3s and 3p. The remaining electrons especially are of spectroscopical interest.

This communication reports the ZEEMAN effect of the strongest *Ni* arc lines, ranged from 4000 to 3000 Å and being combinations of low lying term groups. These low lying term groups arise from the configurations  $3d^8.4s^2$ ,  $3d^9.4s$  and  $3d^9.4p$ , formed by the ten remaining electrons. The terms arising from those configurations are given in the following scheme.

Electronic configuration							Symbol	Terms	
1s	2s	2p	3s	3p	3d	4s	4p	Triplet	Singlet
2	2	6	2	6	8	2		F P	G D S
2	2	6	2	6	9	1		D	D
2	2	6	2	6	9		1	F D P	F D P

Important intensity anomalies in the *Ni* arc spectrum are of interest<sup>2)</sup>.

§ 3. *Preceding observations on the ZEEMAN-effect of Nickel.* Shortly after Prof. ZEEMAN's discovery in 1896 of the influence of the magnetic field on the emission of light REESE<sup>3)</sup> investigated the ZEEMAN effect of several metals and among them of 19 lines of Nickel. REESE's work was

- 1) F. M. WALTERS, J., Wash. Ac. of Sc. 15, 88, 1925.  
K. BECHERT and L. A. SOMMER, Ann. der Phys. 77, 351, 1925.  
K. BECHERT, Ann. der Phys. 77, 538, 1925.  
W. F. MEGGERS and F. M. WALTERS, Sc. Pap. Bur. of Stand. 22, 205, 1927.  
A. C. MENZIES, Phil. Mag. 6, 1210, 1928.  
H. N. RUSSELL, loc. cit.
- 2) L. S. ORNSTEIN and T. BOUMA, Phys. Rev. 36, 679, 1930.
- 3) H. M. REESE, Astr. J. 12, 120, 1900.

continued by KENT<sup>1)</sup>. The resolution obtained by these authors was not large. These first observations have been followed by several others, among which may be mentioned those of PETERKE<sup>2)</sup>, GRAFTDIJK<sup>3)</sup>, TAKAKASHI<sup>4)</sup> and YAMADA<sup>5)</sup>. None of these observations however permits of fixing the  $g$ -values. LÜTTIG<sup>6)</sup> made measurements on lines in the visible part of the spectrum by means of an échelon transmission spectrograph. His measurement of the line 5477 agrees with that given in the present paper. In his paper on the ZEEMAN effect of the Palladium spectrum BEALS<sup>7)</sup> gives reproductions of the Nickel lines 3597 and 3722, both lines showing resolutions in agreement with their classification.

§ 4. *Experimental part.* The magnet used for the present investigation was the same WEISS electromagnet as used in previous investigations in Prof. ZEEMAN's laboratory<sup>8)</sup>. The field strength has been measured in the usual way by means of the ZEEMAN effects of the Zinc triplet 4810, 4722, 4680 and of the Cadmium triplet 5086, 4800, 4679 or of the Aluminium ground doublet 3961, 3944. The field strength amounted to 40.000 Gauss.

As a light source the interrupting spark of a so called "vacuum trembler" = constructed in this laboratory by VAN DER MARK and VAN DER ZWAAL<sup>9)</sup> = has been used. It is a modification of BACK's well known "Abreissbogen", in such a manner that BACK's mechanical arrangement for moving the tungsten electrode has been discarded. A description has been given elsewhere<sup>10)</sup>.

In order to excite the Nickel spectrum the fixed electrode consisted of little bars of the required small dimensions (about  $25 \times 2 \times 2.5$  mm.) sawn out of so called "Bright Ray" being mainly composed of 80 % Ni and 20 % Cr., with impurities of Fe, Cu, etc. This "Bright Ray" has the property that the Nickel in it has lost its ferro magnetic behaviour.

The spark was produced in Hydrogen of low pressure (2 or 3 cm.) that was passing slowly through the vacuum box, enclosing the pole pieces of the magnet. In this way small leakages, which are sometimes inevitable, gave no trouble. The trembler is operated for Ni on 70 Volts dc.

<sup>1)</sup> N. A. KENT, Astr. J. 13, 289, 1901.

Johns Hopkins Un. circ. 20, 82, 1901.

<sup>2)</sup> C. PETERKE, Halle Inaug. Diss., 1909.

<sup>3)</sup> J. M. GRAFTDIJK, Thesis Amsterdam, 1911.

<sup>4)</sup> Y. TAKAKASHI, J. Col. Sc. Tokyō 41, Art. 8, 1921.

<sup>5)</sup> K. YAMADA, J. Col. Sc. Tokyō 41, Art. 870, 1921.

<sup>6)</sup> O. LÜTTIG, Ann. d. Phys. 38, 43, 1912.

<sup>7)</sup> C. S. BEALS, Proc. R. S. London A 109, 369, 1925.

<sup>8)</sup> These Proceedings 31, 780, 1928; 32, 515, 1929; 32, 565, 1929.

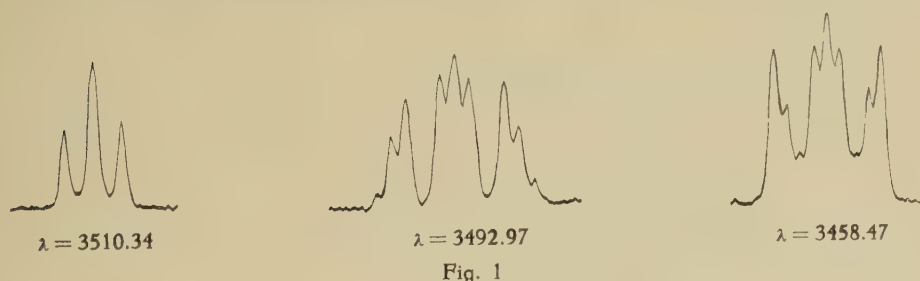
<sup>9)</sup> S. GOUDSMIT, J. V. D. MARK and P. ZEEMAN, Proc. R. S. Amsterdam, 28, 127, 1925.

<sup>10)</sup> C. J. BAKKER, Archives Néerlandaises, serie IIIa, tome XIII, pag. 121, 1931.

A condensing quartz fluorite lens produced an image of the spark on the slit of the grating mounting.

The differently polarized components in the ZEEMAN types were separated by using a calcspar rhomb (thickness 2 cm.) placed before the quartz window of the vacuum box and giving two well separated oppositely polarized images of the spark on the slit of the grating mounting<sup>1)</sup>.

The observations have been made with a large 6 inch Rowland grating, ruled 14.437 lines per inch and with a radius of curvature of 20 feet. The grating was in an Eagle mounting. Nearly all measurements have been made in the 3<sup>rd</sup> order, giving a dispersion of about 0.8 Å mm. Some weak lines have been measured in the 2<sup>nd</sup> order only. The duration of exposure ranged from 10 minuits for strong lines to 3 hours for the weaker lines. Fig. 1 gives photograms of the ZEEMAN effect of 3 lines, showing good



resolution. The photograms are made with a ZEISS photometer with an enlargement of 26:1.

§ 5. *ZEEMAN-Effects of Ni lines.* Table 1 includes the ZEEMAN-effects of Ni lines present on the plates and which are of interest to determine the  $g$ -values of the terms of the configurations  $3d^9.4s$  and  $3d^9.4p$ . The first column gives the wave lengths in Int. Angstrom units taken from HAMM<sup>2)</sup>. The second column denotes the classification according to RUSSELL's paper<sup>3)</sup>. The third column gives the ZEEMAN effects, where

$L$  = ZEEMAN effect calculated after LANDÉ's  $g$ -formula.

obs. = observed ZEEMAN effect.

calc. = ZEEMAN effect calculated with anomalous  $g$ -values.

The fourth column refers to the  $g$ -values according to LANDÉ's formula (LANDÉ) and to those which, according to well known methods, can be calculated from the observed ZEEMAN effects (obs.)<sup>4)</sup>.

It may be noticed that a number of ZEEMAN effects have not been completely resolved. Nevertheless those unresolved types are of interest to show that the observed type is in accordance with the type calculated

1) P. ZEEMAN, *Researches in Magneto-Optics*, Ed. Mac. Millan, pag. 47.

2) S. HAMM, *Zs. f. Wiss. Phot.* 13, 105, 1914.

3) H. N. RUSSELL, loc. cit.

E. BACK IN BACK—LANDÉ, *Zeeman-effekt und Multiplettstruktur*, p. 152—184.

C. J. BAKKER, loc. cit.

TABLE I.

$\lambda$ I. A.	Termcomb. $x-y$	ZEEMAN-effect								$g_x$		$g_y$	
										Landé.	obs.	Landé.	obs.
5476.91	$d^{10} \ ^1S_0-d^9p \ ^1P_1$	L	(0.00)	1.00									
		obs.	(0.00)	1.015						%	%	1.00	1.02
		calc.	(0.00)	1.02									
3858.28	$d^9s \ ^1D_2-d^9p \ ^3F_3$	L	(0.00)	(0.08)	(0.17)	0.92	1.00	1.08	1.17	1.25			
		obs.	(0.00)						1.16			1.00	1.01
		calc.	(0.00)	(0.07)	(0.14)	0.94	1.01	1.08	1.15	1.22		1.08	1.08
3775.56	$d^9s \ ^1D_2-d^9p \ ^3D_2$	L	(0.17)	(0.33)	0.83	1.00	1.17	1.34					
		obs.	(0.00)				1.03					1.00	1.01
		calc.	(0.02)	(0.04)	0.99	1.01	1.03	1.05				1.17	1.03
3664.09	$d^8s^2 \ ^3F_2-d^9p \ ^3P_1$	L	(0.00)	(0.83)	0.17	0.67	1.50						
		obs.	(0.00)	(0.76)	0.00	0.68						0.67	0.67
		calc.	(0.00)	(0.76)	0.09	0.67	1.43					1.50	1.43
3619.39	$d^9s \ ^1D_2-d^9p \ ^1F_3$	L	(0.00)	100									
		obs.	(0.00)					1.07				1.00	1.01
		calc.	(0.00)	(0.03)	(0.06)	0.98	1.01	1.04	1.07	1.10		1.00	1.04
3612.73	$d^8s^2 \ ^3F_2-d^9p \ ^3D_2$	L	(0.50)	(1.00)	0.17	0.67	1.17	1.67					
		obs.	—	(0.73)	—	0.68	1.05	—				0.67	0.67
		calc.	(0.36)	(0.73)	0.30	0.67	1.03	1.39				1.17	1.03
3610.45	$d^9s \ ^3D_2-d^2p \ ^3P_2$	L	(0.33)	(0.67)	0.83	1.17	1.50	1.83					
		obs.	(0.33)	(0.67)	0.82	1.15	1.49	1.83				1.17	1.15
		calc.	(0.34)	(0.68)	0.81	1.15	1.49	1.83				1.50	1.49
3597.70	$d^9s \ ^3D_1-d^9p \ ^3P_1$	L	(1.00)	0.50	1.50								
		obs.	(0.93)	0.50	1.43							0.50	0.50
		calc.	(0.93)	0.50	1.43							1.50	1.43
3571.87	$d^8s^2 \ ^3F_3-d^9p \ ^3F_3$	L	(0.00)	1.08									
		obs.	(0.00)	1.08								1.08	1.08
3566.37	$d^9s \ ^1D_2-d^9p \ ^1D_2$	L	(0.00)	1.00									
		obs.	(0.07)			1.035						1.00	1.01
		calc.	(0.05)	(0.0)	0.96	1.01	1.06	1.11				1.00	1.06
3524.54	$d^9s \ ^3D_3-d^9p \ ^3P_2$	L	(0.00)	(0.17)	(0.33)	1.00	1.17	1.33	1.50	1.67			
		obs.	(0.00)	(0.15)	(0.30)	1.02	1.17	1.33	—	—		1.33	1.33
		calc.	(0.00)	(0.15)	(0.31)	1.02	1.17	1.33	1.49	1.65		1.50	1.49
3515.06	$d^9s \ ^3D_2-d^9p \ ^3F_3$	L	(0.00)	(0.08)	(0.17)	0.92	1.00	1.08	1.17	1.25			
		obs.	(0.00)				1.02					1.17	1.15
		calc.	(0.00)	(0.07)	(0.14)	0.94	1.01	1.08	1.15	1.22		1.08	1.08
3510.34	$d^9s \ ^3D_1-d^9p \ ^3P_0$	L	(0.00)	0.50									
		obs.	(0.00)	0.50								0.50	0.50
3500.85	$d^8s^2 \ ^3F_3-d^9p \ ^3D_2$	L	(0.00)	(0.08)	(0.17)	0.92	1.00	1.08	1.17	1.25			
		obs.	(0.00)						1.12			1.08	1.08
		calc.	(0.00)	(0.05)	(0.10)	0.98	1.03	1.08	1.13	1.18		1.17	1.03
3492.97	$d^9s \ ^3D_2-d^9p \ ^3P_1$	L	(0.00)	(0.33)	0.83	1.17	1.50						
		obs.	(0.00)	(0.27)	0.87	1.15	1.43					1.17	1.15
		calc.	(0.00)	(0.28)	0.87	1.15	1.43					1.50	1.43



TABLE I (Continued)

$\lambda$ I.A.	Termcomb. x—y	ZEEMAN-effect									g <sub>x</sub>		g <sub>y</sub>		Remarks	
											Landé.	obs.	Landé.	obs.		
3483.78	d <sup>8</sup> s <sup>2</sup> <sup>3</sup> F <sub>2</sub> —d <sup>9</sup> p <sup>3</sup> D <sub>1</sub>	L	(0.00)	(0.17)	0.50	0.67	0.83									
		obs.	(0.00)			0.76					0.67	0.67	0.50	0.55	16)	
		calc.	(0.00)	(0.12)	0.55	0.67	0.97									
3472.55	d <sup>9</sup> s <sup>3</sup> D <sub>2</sub> —d <sup>9</sup> p <sup>3</sup> D <sub>3</sub>	L	(0.00)	(0.17)	(0.33)	1.00	1.17	1.33	1.50	1.67						
		obs.	(0.00)						1.55		1.17	1.15	1.33	1.29	17)	
		calc.	(0.00)	(0.14)	0.28)	1.01	1.15	1.29	1.43	1.57						
3458.47	d <sup>9</sup> s <sup>3</sup> D <sub>1</sub> —d <sup>9</sup> p <sup>3</sup> F <sub>2</sub>	L	(0.00)	(0.17)	0.50	0.67	0.83									
		obs.	(0.00)	(0.24)	0.50	0.74	0.98				0.50	0.50	0.67	0.74	18)	
		calc.	(0.00)	(0.24)	0.50	0.74	0.98									
3446.26	d <sup>9</sup> s <sup>3</sup> D <sub>2</sub> —d <sup>9</sup> p <sup>3</sup> D <sub>2</sub>	L	(0.00)	1.17												
		obs.	0.20			1.09					1.17	1.15	1.17	1.03	19)	
		calc.	(0.12)	(0.24)	0.91	1.03	1.15	1.27								
3423.71	d <sup>9</sup> s <sup>3</sup> D <sub>1</sub> —d <sup>9</sup> p <sup>3</sup> D <sub>1</sub>	L	(0.00)	0.50												
		obs.	(0.00)	0.52 <sup>5</sup>							0.50	0.50	0.50	0.55	20)	
		calc.	(0.05)	0.50	0.55											
3414.77	d <sup>9</sup> s <sup>3</sup> D <sub>3</sub> —d <sup>9</sup> p <sup>3</sup> F <sub>4</sub>	L	(0.00)	0.08)	0.17)	(0.25)	1.00	1.08	1.17	1.25	1.33					
		obs.	(0.00)					1.16		[1.42	1.50	1.33	1.33	1.25	1.25	21)
3392.99	d <sup>9</sup> s <sup>3</sup> D <sub>3</sub> —d <sup>9</sup> p <sup>3</sup> D <sub>3</sub>	L	(0.00)	1.33												
		obs.	(0.00)					1.30 <sup>5</sup>				1.33	1.33	1.33	1.29	22
		calc.	(0.04)	(0.09)	(0.13)	1.20	1.25	1.29	1.33	1.38	1.42					
3391.05	d <sup>8</sup> s <sup>2</sup> <sup>3</sup> F <sub>4</sub> —d <sup>9</sup> p <sup>3</sup> F <sub>4</sub>	L	(0.00)	1.25												
		obs.	(0.00)	1.25								1.25	1.25	1.25	1.25	23)
3380.58	d <sup>9</sup> s <sup>1</sup> D <sub>2</sub> —d <sup>9</sup> p <sup>1</sup> P <sub>1</sub>	L	(0.00)		1.00											
		obs.	(0.00)		1.01							1.00	1.01	1.00	1.02	24)
		calc.	(0.00)	(0.01)	1.00	1.01	1.02									
3369.58	d <sup>8</sup> s <sup>2</sup> <sup>3</sup> F <sub>4</sub> —d <sup>9</sup> p <sup>3</sup> D <sub>3</sub>	L	(0.00)	(0.08)	(0.17)	(0.25)	1.00	1.08	1.17	1.25	1.33					
		obs.	(0.00)					1.19		[1.42	1.50	1.25	1.25	1.33	1.29	25)
		calc.	(0.00)	(0.04)	(0.08)	(0.12)	1.13	1.17	1.21	1.25	1.29					
										[1.31	1.37					

## REMARKS.

- 1) Sharp triplet. In 2<sup>nd</sup> order only.
- 2) Shows correct type. In 2<sup>nd</sup> order only.
- 3) Sharp triplet. In 2<sup>nd</sup> order only.
- 4) Observed  $\sigma$ -comp. 0.00 is clearly enlarged. In 2<sup>nd</sup> order only.
- 5) Shows correct type.
- 6) In 3<sup>rd</sup> order the strong  $\pi$ -comp. 0.73 could be measured only. Both the obs.  $\pi$ -comp. have been measured in 2<sup>nd</sup> order.
- 7) In 3<sup>rd</sup> order all  $\pi$ -comp. and two strongest  $\sigma$ -comp. could be measured. In 2<sup>nd</sup> order all  $\sigma$ -comp. are present.
- 8) Sharp sextet.
- 9) Sharp triplet.
- 10) All components are enlarged.
- 11) Well resolved type. The weakest  $\sigma$ -comp. could not be measured.
- 12) Shows the correct type.
- 13) Sharp triplet. See Fig. 1.
- 14) Shows the correct type.
- 15) Well resolved type. See Fig. 1.
- 16) Weak in 3<sup>rd</sup> order.
- 17) Shows the correct type. Weak in 3<sup>rd</sup> order.
- 18) Well resolved type. See Fig. 1.
- 19) All components are enlarged.
- 20) Rather sharp triplet.
- 21) Shows the correct pseudo-triplet type.
- 22) All components are enlarged.
- 23) Sharp triplet.
- 24) Sharp triplet.
- 25) Shows the correct pseudo-triplet type.



with the aid of the  $g$ -values determined from other combinations. The line  $3500.85\ d^8.s^2\ ^3F_3-d^9.p\ ^3D_2$  is an example of this. The ZEEMAN effect calculated according to LANDÉ's formula would show  $\sigma$ -components, if unresolved, with decrease of intensity to the outside. The ZEEMAN effect calculated by means of  $g=1.08$  for  $d^8.s^2\ ^3F_3$  and  $g=1.03$  for  $d^9.p\ ^3D_2$ , both  $g$ -values determined from other lines, shows  $\sigma$ -components, if unresolved, with decrease of intensity to the inside. The latter is really observed. Secondly it sometimes is possible to deduce from an unresolved type, if the  $g$ -value of one of the combining terms is known, the  $g$ -value of the other term with considerable accuracy<sup>1)</sup>.

In the spectral region investigated separations less than 0.15 times the normal magnetic separation distance could not be resolved, so causing the observed  $g$ -values in most cases to have an uncertainty of 0.01.

The last column in table 1 contains the remarks to the observed types. If an observed and unresolved type is in accordance with the calculated type, as to decrease of intensity in the components it is remarked that it shows the correct type. If the ZEEMAN effect of a line has been observed in the 2<sup>nd</sup> order only it is especially noted.

It is well known that the ZEEMAN effect can show whether a spectral line is masked by another one. This is clearly observed in the *Ni* spectrum for the lines 3674.11, 3548.19 and 3433.57. These lines are also given in RUSSELL's list with double interpretation.

§ 6. Table II and III include the terms of the configurations  $d^9.s$  and  $d^9.p$ . For those configurations the  $g$ -values of the whole set of terms could be determined. The relative termvalues, given in column 2, refer to a value 0.00 for the term  $d^8.s^2\ ^3F_4$ , which is the lowest lying term in the Nickel arc spectrum. The absolute term values can be obtained by adding 61579 to the relative term values in accordance with RUSSELL's datum of the ionisation potential of *Ni* I (7.6 Volts).

TABLE II.

Term	Relative term value	Term difference	$g$ -values	
			LANDÉ	Observed
$d^9.s\ ^3D_3$	204.82	675.00	1.333	1.33
$d^9.s\ ^3D_2$	879.82		1.166	1.15
$d^9.s\ ^3D_1$	1713.11	833.29	0.500	0.50
$d^9.s\ ^1D_2$	3409.95		1.000	1.01

<sup>1)</sup> A. G. SHENSTONE and H. A. BLAIR, *Phil. Mag.* 8, 765, 1929.

TABLE III.

Term	Relative term value	Term difference	g-values	
			LANDÉ	Observed
$d^9p\ ^3P_2$	28569.30	931.45 691.55	1.500	1.49
$d^9p\ ^3P_1$	29500.75		1.500	1.43
$d^9p\ ^3P_0$	30192.30		0/0	0/0
$d^9p\ ^3F_4$	29480.96	-160.21 1298.65	1.250	1.25
$d^9p\ ^3F_3$	29320.75		1.083	1.08
$d^9p\ ^3F_2$	30619.40		0.666	0.74
$d^9p\ ^3D_3$	29668.89	219.58 1024.40	1.333	1.29
$d^9p\ ^3D_2$	29888.47		1.166	1.03
$d^9p\ ^3D_1$	30912.87		0.500	0.55
$d^9p\ ^1F_3$	31031.02		1.000	1.04
$d^9p\ ^1D_2$	31441.64		1.000	1.06
$d^9p\ ^1P_1$	32982.30		1.000	1.02

A quantum mechanics perturbation theory may be applied, according to LAPORTE and INGLIS<sup>1)</sup>, to the terms of the configuration  $d^9s$ . From the position of the terms the  $g$ -values  $g^3D_2=1.152$  and  $g^3D_1=1.015$

TABLE III. Configuration  $(3d)^9 4s$ .

(SL) coupling		NiI		(JJ) coupling	
Term	Calc. g-value	Obs. g-value	Calc. g-value	Structure	
J = 3 $^3D_3$	1.333	1.33	1.333	$-d_{3/2} + s_{1/2}$	
J = 2    {	$^3D_2$	1.166	1.15	1.100	$-d_{3/2} + s_{1/2}$
	$^1D_2$	1.000	1.01	1.066	$-d_{3/2} + s_{1/2}$
	g-sum	2.166	2.16	2.166	
J = 1 $^3D_1$	0.500	0.50	0.500	$-d_{3/2} + s_{1/2}$	

<sup>1)</sup> O. LAPORTE and D. R. INGLIS, Phys. Rev. 35, 1340, 1930.

are calculated. The experimental  $g$ -values are in good agreement with these calculated values as may be seen from table II.

In table III and IV the terms are arranged in such a way that terms of equal value of the total impulse moment  $J$  are grouped together. According to PAULI's  $g$ -sum rule one expects that the sum of the  $g$ -values of the terms of such a group is independent of the coupling which is involved. Therefore this sum must be equal to the sum of LANDÉ's  $g$ -values for these terms. It is seen that within the experimental errors this rule holds very well.

The last column shows the  $g$ -values calculated for ( $JJ$ ) coupling. The structure has been taken from MACK<sup>1)</sup>, who derived it from the compa-

TABLE IV. Configuration  $(3d)^9 4p$ .

(SL) coupling		Ni I		(JJ) coupling
Term	Calc. $g$ -value	Obs. $g$ -value	Calc. $g$ -value	Structure
$J = 4$ $^3F_4$	1.250	1.25	1.250	$-d_{5/2} + p_{3/2}$
$J = 3$ $\left\{ \begin{array}{l} ^3F_3 \\ ^3D_3 \\ ^1F_3 \end{array} \right.$	1.083	1.08	1.111	$-d_{5/2} + p_{1/2}$
	1.333	1.29	1.239	$-d_{5/2} + p_{3/2}$
	1.000	1.04	1.066	$-d_{3/2} + p_{3/2}$
	+	+	+	
$g$ -sum	3.416	3.41	3.416	
$J = 2$ $\left\{ \begin{array}{l} ^3P_2 \\ ^3F_2 \\ ^3D_2 \\ ^1D_2 \end{array} \right.$	1.500	1.49	1.289	$-d_{5/2} + p_{1/2}$
	0.666	0.74	1.211	$-d_{5/2} + p_{3/2}$
	1.166	1.03	0.766	$-d_{3/2} + p_{1/2}$
	1.000	1.06	1.066	$-d_{3/2} + p_{3/2}$
	+	+	+	
$g$ -sum	4.332	4.32	4.332	
$J = 1$ $\left\{ \begin{array}{l} ^1P_1 \\ ^3P_1 \\ ^3D_1 \end{array} \right.$	1.000	1.02	1.100	$-d_{5/2} + p_{3/2}$
	1.500	1.43	0.834	$-d_{3/2} + p_{1/2}$
	0.500	0.55	1.066	$-d_{3/2} + p_{3/2}$
	+	+	+	
$g$ -sum	3.000	3.00	3.000	
$J = 0$ $^3P_0$	0/0	0/0	0/0	$-d_{3/2} + p_{3/2}$

<sup>1)</sup> J. E. MACK, Phys. Rev. 34, 17, 1929.

rison of the iso electronic systems *Ni* I, *Cu* II, *Zn* III, *Ga* IV and *Ge* V. For *Ni* I the *g*-values interpose between the LANDÉ *g*-values and those calculated according to (*JJ*) coupling, as may be seen from the tables.

The author is indebted to Prof. ZEEMAN for his interest and advice during this investigation.

*Laboratory "Physica" of the University.*

*Amsterdam, Jan. 1932.*

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**Physics.** — *An X-ray Investigation of the n-mono-alkyl malonic Acids.*

By D. COSTER and A. V. D. ZIEL. (Communicated by Prof. J. G. VAN DER CORPUT.)

(Communicated at the meeting of January 30, 1932.)

As is well known, several series of organic compounds (fatty acids, paraffines) when investigated by X-rays, show the existence of a long spacing which increases proportionally to the number of C-atoms in the molecule. Very often in those compounds a phenomenon of alternation has been observed: the spacing of the molecules with an odd number of C-atoms not lying midway between the spacings of the adjacent molecules with an even number of C-atoms, but those with an even number as well as those with an odd number of C-atoms forming a series of their own. Also as regards other properties: melting point, solubility, heat of combustion, analogous alternating phenomena have been observed<sup>1)</sup>.

Prof. VERKADE at Rotterdam proposed us to investigate by means of X-rays a series of *n*-mono-alkyl malonic acids used in his own work in order to make sure in how far a parallelism between the change in grating constant in this series and other properties investigated by him exists.

The work was done with a vacuumspectrograph of a slightly modified type. The crystal table was fixed to the cover of the spectrograph. This cover turned with a cone on the body of the spectrograph, its position could be read on a scale with a vernier. The distance from the slit to the axis of the spectrograph or from the axis to the photographic plate was 6,18 cm. The preparation was brought in a thin sheet on a glass strip which was fixed on the crystal table. The thin sheet was made by first dissolving the substance in water (the lower members of the series) or in alcohol, acetone or ether (the higher members) and pouring a little of the solution on the glass strip. The thickness of the sheet which remained after

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<sup>1)</sup> See e.g. P. E. VERKADE, H. HARTMAN and J. COOPS, *Rec. trav. chim. Pays Bas*, **45**, 373; 1926.

P. E. VERKADE, J. COOPS and H. HARTMAN, *ibidem* **45**, 545, 1926.

P. E. VERKADE and J. COOPS, *ibidem* **46**, 903, 1927.

P. E. VERKADE and J. COOPS, *ibidem* **49**, 568, 1930.

the liquid was evaporated was not more than 0,1 mm. This sheet of the preparation works as a reflecting crystal in the BRAGG camera. It was first brought in the axis of the spectrograph, the zero position was determined, then it was turned into the right position for reflection. During the exposure it was oscillated over an angle of about  $0,3^\circ$  on both sides of the angle of BRAGG reflection. As the glass strip was always fixed in the same way on the crystal table, the adjustment as well as the determination of the zero position had only to be done once.

The grating constants were calculated from the first and second order spectral lines at the same side of the direct beam. In order to control the identification of the spectral lines, also the first order reflections on both sides of the direct beam were taken on another plate. The lines were in general less sharp than those obtained by the same method with fatty acids. This means that the individual crystals are not so well oriented with their reflecting planes parallel to the surface of the glass as in the case of the fatty acids. Therefore it was necessary to make the beam of X-rays very narrow (the divergence of the beam was not more than  $\frac{1}{2}$  degree) so that the reflection takes place only on a small part of the preparation in the neighbourhood of the axis of the spectrograph.

The results are given in table 1 and Fig. 1.

TABLE 1.

$C_n H_{2n+1} CH(COOH)_2$		Grating constant	
			Value of HENDERSON
$n = 1$	methyl	5.07 Å U	
2	ethyl	7.25 „ „	7.36
3n	propyl	8.50 „ „	8.70
4n	butyl	9.71 „ „	9.83
5n	amyl	10.82 „ „	
6n	hexyl	12.09 „ „	
7n	heptyl	12.44 „ „	12.78
8n	octyl	14.38 „ „	
9n	nonyl	14.61 „ „	
10n	decyl	16.64 „ „	
11n	undecyl	16.82 „ „	
12n	dodecyl	18.90 „ „	
13n	tridecyl	19.09 „ „	
14n	tetradecyl	21.15 „ „	



We estimate the accuracy of our numbers to be about 3 ‰ for the members of the series higher than  $C_5$  and about 5 ‰ for the lower ones, where the lines are still more diffuse.

In the third column the values found by HENDERSON<sup>1)</sup> are inserted. They differ slightly more from our values than the limit of experimental error for our numbers. Besides HENDERSON has measured  $C_{18}$ , for which he finds 25.59 Å, in good agreement with the value 25.67 extrapolated from our numbers. From his data HENDERSON has already drawn the conclusion, that in the case of the *n*-mono-alkyl malonic acids there is only one molecule between successive reflecting planes. This conclusion is confirmed by table 1. For the higher members of the series the spacing increases on the average with 1.13 Å per  $CH_2$ -group, whereas in the case of the fatty acids, where two molecules are supposed to be between two successive identity planes, this increase is about 2.3 Å. From this the conclusion may be drawn that in the case of the *n*-mono-alkyl malonic acids the two active carboxyl groups of the same molecule are saturated by one

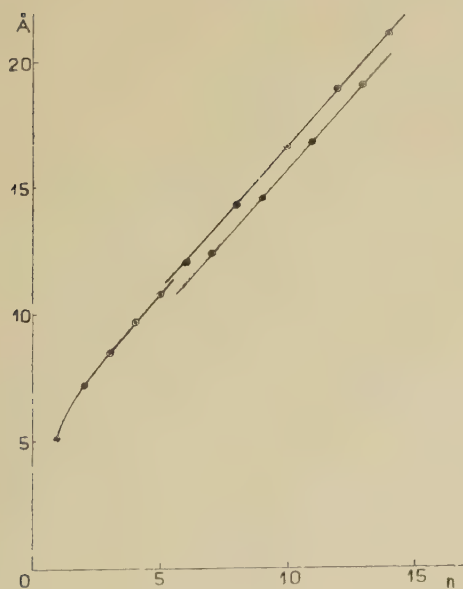


Fig. 1

The grating constant as a function of the number of C-atoms in the alkyl group of the *n*-mono-alkyl malonic acids.

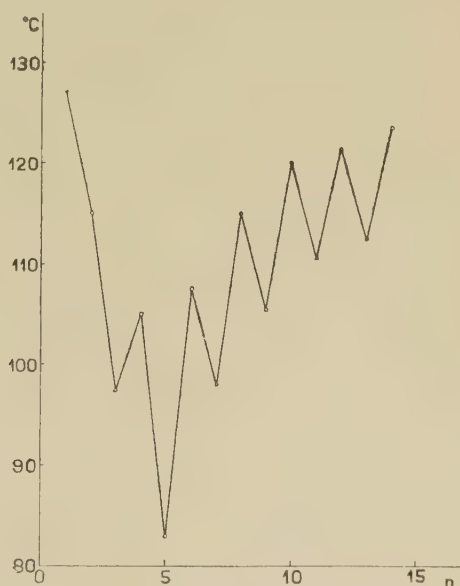


Fig. 2

Melting point of the *n*-mono-alkyl malonic acids as a function of the number of C-atoms in the alkyl-group.

another, whereas in the case of the fatty acids, where two molecules are placed head-on between the identity planes, the carboxyl groups of two successive molecules are saturated by one another.

Fig. 1 reveals a new interesting fact: beginning with  $C_6$  the higher

<sup>1)</sup> E. HENDERSON, Proc. Roy. Soc. of Edinburgh 48, 20, 1927-'28.

members of the series show the phenomenon of alternation in grating constant for the odd and even numbers as discussed above. The lower members, however, do not show such alternation; they form a series of their own which is different from the odd as well as from the even higher members. It is a very curious fact that the lower members of the series cannot be regarded as a continuation of the higher members, the latter forming a series beginning with  $C_6$ . The same feature is also shown by other physical properties. This is clearly brought out by the figures 2, 3 and 4. The data with the help of which these figures were constructed are taken from the work of VERKADE and COOPS<sup>1)</sup>. Fig. 2 shows an alternating series with a melting point increasing on the average for the higher members beginning with  $C_6$ , whereas the lower members form a series of their own with a melting point decreasing on the average as the number of C-atoms increases.

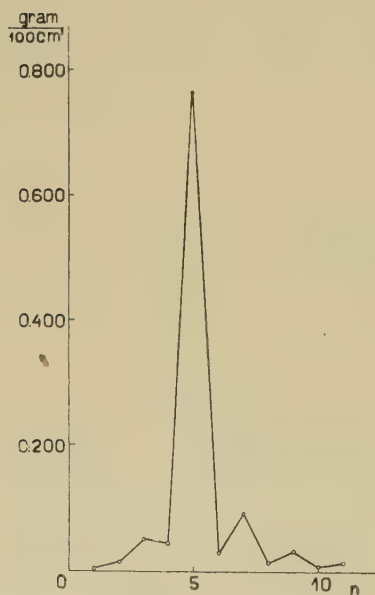


Fig. 3

Solubility of the *n*-mono-alkyl malonic acids in benzene as a function of the number of C-atoms in the alkyl group.

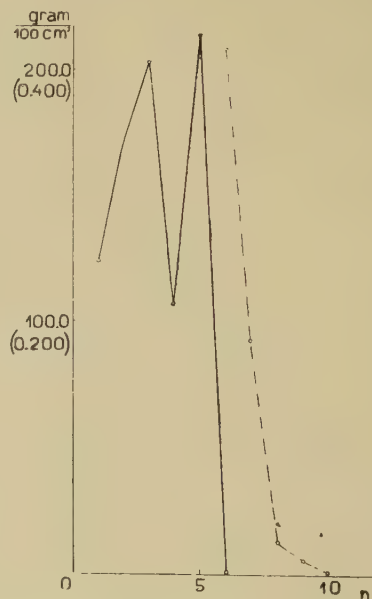


Fig. 4

Solubility of the *n*-mono-alkyl malonic acids in water as a function of the number of C-atoms in the alkyl group. As the solubility for the higher members beginning with  $C_6$  is very small, for these the curve is drawn on a larger scale (dotted line).

An analogous aspect is met in Fig. 3. The higher members form an alternating series beginning with  $C_6$  with on the average decreasing solubility in benzene as the number of C-atoms increases. With the lower mem-

<sup>1)</sup> P. E. VERKADE and J. COOPS, Rec. trav. chim. Pays Bas **49**, 568, 1930.

bers, however, on the average the solubility increases as the number of C-atoms increases. An anomalously large maximum is shown by  $C_5$ .

A slightly different behaviour for the solubility in water is shown in Fig. 4. Here the phenomenon of alternation is not shown by the higher members, but they behave also quite differently from the lower members in as much as the solubility is very great for the latter ones and very small for the former ones.

As is seen from Fig. 1 the grating constant of methyl malonic acid is smaller than the value obtained by a linear extrapolation from the constants for the acids  $C_2$ ,  $C_3$ ,  $C_4$  and  $C_5$ . Also in other respects  $C_1$  behaves different from the other lower members of the series. From Fig. 2 e. g. we see that in general the lower as well as the higher members alternate in melting point. If  $C_1$  should do the same, its melting point had to be lower than that of  $C_2$  whereas as a matter of fact it is higher. An analogous conclusion may be drawn as regards the solubility (see Fig. 3 and 4). It therefore seems, that  $C_1$  hardly belongs to the series of the lower members, but that this series only begins with  $C_2$ .

The preparations of Prof. VERKADE appeared to be very pure. At any rate, in general, no other long spacings were found than those inserted in table 1. An exception will be discussed further on. The lines which appeared most clearly on the plates were the copper  $K\alpha$  and  $K\beta$  lines (a copper antikathode was used in the X-ray tube). As a tungsten hot wire kathode was used and the tungsten was sputtered on the antikathode, also the  $La$  and  $L\beta$ -lines of tungsten appeared on the plates but usually rather weak. The lines are clearly seen on the photometercurves (see Fig. 5). Because of the small dispersion the  $La$ -line of tungsten is not separated from the  $Cu K\alpha$  line; it is only seen as an asymmetry in the latter <sup>1)</sup>. For the same reason the  $L\beta_1$  and  $L\beta_2$  line of tungsten could not be separated. The large blackening to the right is the direct beam. Between this and the lines already referred to, very often another group of lines of variable intensity is found. They point at a grating constant about two times as large as those of table 1.

Now it is well known that many organic acids are decomposed under the influence of light <sup>2)</sup>. Malonic acid e.g. decomposes into acetic acid and carbon dioxide <sup>3)</sup>. To test this point for the acids in this paper we mounted a strip of glass with a certain preparation, say  $C_8$ , in the X-ray spectrograph and determined the spectrum. Then the preparation was exposed to the mercury arc or to sunlight, and again an X-ray spectrum was taken. To make sure that the same part of the preparation was responsible for the X-ray spectrum before and after the treatment by light, the cover of the spectrograph with the crystal table was taken from the

<sup>1)</sup> Naturally the dispersion is far too small to separate the two components of the  $K\alpha$ -line.

<sup>2)</sup> See KISTIAKOWSKY "Photochemical Processes" The Chemical Catalog Co. Inc. New York 1928, p. 146, 229.

<sup>3)</sup> VOLMAR, Compt. Rend. **180**, 1172, 1925.

X-ray spectrograph for this treatment and care was taken that nothing in the adjustment of the glass strip with the preparation was changed. The Fig. 5, 6, 7 and 8 are photometercurves taken from spectra made with the same preparation  $C_8$  in the same position but respectively exposed to sunlight or the light of the mercury arc.

From the Fig. 5, 6, 7 and 8 it is clearly shown that the *n*-mono-alkyl malonic acid  $C_8$  gradually changes by photochemical reaction into another substance with much larger grating constant. A comparison of Fig. 7 and Fig. 8 shows that sunlight with a lower limit of wave-length of about  $3300 \text{ \AA}$  works equally well as the mercury quartz arc in which much shorter wave-lengths play an important part. The rather small difference between fig. 5 and 6, though a vigorous treatment with light took place before the spectrum 6 was taken, is a little surprising at first. The same we observed in all other cases, where we studied the photochemical reaction in this way: In the beginning the change takes place very slowly, if once however, the new spacing is a little stronger, then it grows more intense in a comparatively short time. It seems to us that this peculiarity is caused by the method itself. We may assume that in the beginning the photochemical reaction will take place at random throughout the preparation just were a light quantum happens to be absorbed. But by the method of X-ray reflection no single molecule can be detected but only crystalline aggregates of several thousands of molecules of the same kind. We thus understand why in the beginning the new grating appears so slowly; it is because there are perhaps many single molecules but not enough crystalline aggregates to give good reflections.

On the other hand it is a curious fact, indeed, that the lines of the anomalous large spacing as well as of the old normal spacing are rather sharp on fig. 7 and 8. From this we may conclude that the individual crystals which give rise to the reflections in question must not be too small (say at least hundred reflecting planes). This curious fact proves that the molecules with anomalous large grating are not distributed at random between the original molecules, but are more or less concentrated in rather large aggregates. So far as we see, this may be explained in two different ways: It is possible that they are formed at random throughout the substance and by diffusion combine to larger aggregates. Or it might be that the new molecule acts as a kind of catalyser for the photochemical reaction in question. The first supposition seems us to be the most probable.

The same photochemical process was studied in the same way with  $C_{13}$ ,  $C_{12}$  and  $C_{11}$ . As the results were *mutatis mutandis* the same, we need not to go into further detail. As the cause of the appearance of the anomalous large grating now was known, we worked with the preparations in the dark. In this case we really succeeded in getting photographs without the anomalous large spacings.

Another question is, if the X-rays themselves show a photochemical

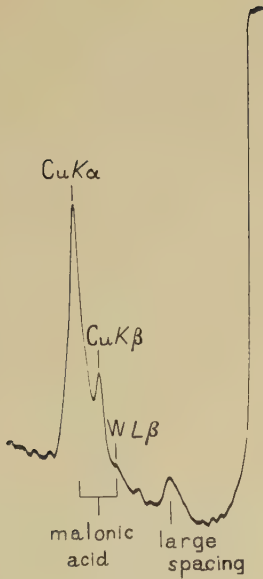


Fig. 5

Before the treatment with light. The anomalous long spacing is visible, but rather weak.

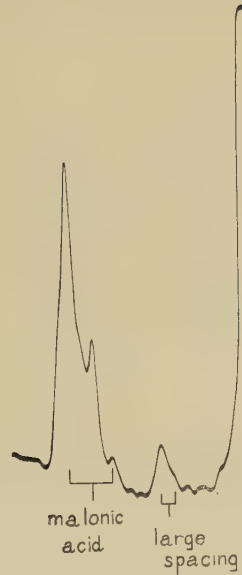


Fig. 6

Exposed during 5 hours to sunlight. The anomalous long spacing is a little stronger, but not much.



Fig. 7

Again exposed during 6 hours to the light of the mercury arc. The anomalous long spacing is much stronger.



Fig. 8

Again exposed during 10 hours to sunlight. The anomalous long spacing gives now by far the strongest reflection. The normal spacing gives much weaker reflections than in the former figures.



action on the alkyl malonic acids. To decide this question we used a preparation of  $C_{11}$  which showed in addition to the normal spacing also the large spacing. The preparation was strongly exposed during 8 hours to  $X$ -rays. A new  $X$ -ray spectrum clearly showed an increase of the intensity of the long spacing. To make sur that no other unknown effect might cause the chemical reaction in question, the preparation was afterwards kept during 15 hours in the dark. An  $X$ -ray spectrum now taken showed no perceptable increase of the intensity of the long spacing.

During one single exposition of an  $X$ -ray spectrum, however, the photochemical action of the  $X$ -rays is too small to give a perceptable effect. The time of exposure is only 2 hours, whereas the  $X$ -rays strike the preparation at an angle of about 1—3 degree. Therefore we estimate the total intensity only about 5 per cent of the intensity in the above case in which a change caused by the  $X$ -rays was clearly observed.

Now the question arises into which substances the  $n$ -mono-alkyl malonic acids are converted by the action of light. As the new substance has a spacing about two times as large as the corresponding alkyl malonic acid, it seems to be most probable that this should be a fatty acid. This seems to be most reasonable also from a chemical point of view. So we might suppose that the octyl malonic acid  $C_8$  is converted into caprinic acid  $C_{10}$  and carbon dioxide.

Unfortunately there are some serious difficulties in testing this question by a measurement of the spacings. As is well known the fatty acids occur in at least 3 different modifications with widely varying grating constants<sup>1)</sup>. Furthermore it seems that the grating constant can be easily changed to a perceptable amount by small impurities or by mechanical treatment of the preparation. Now the values found for the large spacings, which arise from the treatment with light, differ more from the spacings of the fatty acids than the limit of experimental error. In general they are about 10 per cent too small. For the moment we cannot explain this discrepancy but we intend to investigate this point in a continuation of our work.

In conclusion, we wish to express our thanks to Prof. P. E. VERKADE of Rotterdam for supplying the substances investigated in this paper.

*Groningen, Natuurkundig Laboratorium der  
Rijks-Universiteit.*

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<sup>1)</sup> G. M. DE BOER, Nature 119, 634, 1927.

**Physics.** — *Measurement of the piezo-electric modulus of zincblende.*  
By K. S. KNOL. (Communicated by Prof. J. G. VAN DER CORPUT.)

(Communicated at the meeting of January 30, 1932.)

§ 1. In connection with an investigation of the influence of polarity on the intensity of *X*-ray reflection in the case of zincblende, a qualitative determination of the piezo-electric modulus for this substance has been made in this laboratory<sup>1)</sup>. For this constant one finds quoted in the german literature the following value<sup>2)</sup> :

$$\delta_{14} = -5.24 \cdot 10^{-8} \text{ c. g. s. units,}$$

which has been taken from the thesis of L. W. E. VAN DER VEEN<sup>3)</sup>. We have already pointed to the fact that apparently the above number is due to a misunderstanding of VAN DER VEEN's thesis, and that the real value taken from VAN DER VEEN ought to be  $\sqrt{3}$  times as large :

$$\delta_{14} = 9.08 \cdot 10^{-8} \text{ c. g. s. units, } ^4)$$

whereas the negative sign has no meaning at all, as long as no definite agreement has been made about the positive direction in the crystal (Compare § 4).

It seemed worth while to make an absolute redetermination of the piezo-electric modulus of zincblende, in order to make sure in how far the correction proposed by us to the ordinarily quoted value is trustworthy.

From new measurements, which will be discussed below, it follows that the piezo-electric modulus for zincblende is :

$$\delta_{14} = 9.70 \pm 0.15 \cdot 10^{-8} \text{ c. g. s. units.}$$

At the same time I have made a remeasurement of the piezo-electric constant of quartz. For this I find a value about 1 per cent less than the best known values of CURIE and RÖNTGEN. If this discrepancy has to be ascribed to some error in the apparatus (e.g. too small a value, assumed for the electrostatic capacity used in my measurements), then we have to assume that the best value for zincblende is probably :

$$\delta_{14} = 9.80 \cdot 10^{-8} \text{ c. g. s. units,}$$

which is nearly two times as large as the value hitherto quoted.

<sup>1)</sup> D. COSTER, K. S. KNOL and J. A. PAINS, *Zs. f. Phys.* **63**, 345, 1930. Further on quoted as l.c.

<sup>2)</sup> See e.g. *Handb. d. Phys.* (GEIGER u. SCHEEL) XIII page 312.

<sup>3)</sup> L. W. E. VAN DER VEEN, doctor dissertation, Delft 1911.

<sup>4)</sup> From VAN DER VEEN's numbers, as a matter of fact, a value 10 per cent smaller is obtained, but he made his measurements relative to the piezo-electric constant of quartz for which an old value of CURIE, 10 per cent less than the best value of to-day, was taken.

§ 2. The measurements were made with a very simple apparatus, an idea of which may be obtained from figure 1. The crystal was put between two flat polished copperplates of about 3 mm thickness. These plates as well as the crystal itself were cleaned with the utmost care and dried in the exsiccator before they were put together in the box *B* (See figure 1).

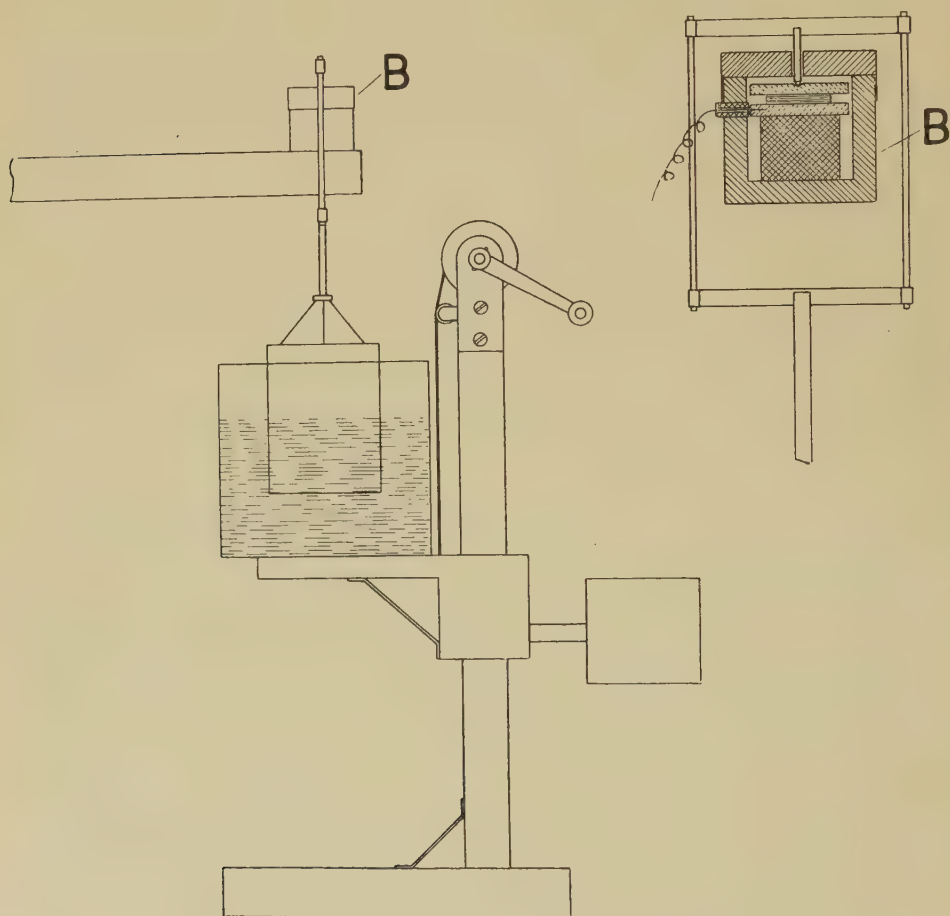


Fig. 1. Apparatus for piezo-electric measurements.

Of this box an enlargement is shown in the upper right hand corner of the figure. It is made of tinned iron. On the bottom lies first a piece of ambroid for insulation, then follows the undermost copperplate of which the electric potential has to be measured with the electrometer, then the piezo-electric crystal and finally the uppermost copperplate. To avoid an eventual pyro-electric effect, care was taken that during the course of one experiment the temperature did not change noticeably. Therefore the box was put in a second one, the space between them being filled with cotton wool.

Furthermore care was taken that all the metal parts of the apparatus with the exception of the undermost copperplate, of which the changes in

potential had to be measured, were constantly grounded. An insulated copperwire connected the undermost copperplate with the string electrometer and (eventually) a capacity of known magnitude. The pressure was furnished by a known weight which pressed through a hole in the cover of the box on the upper copperplate. The difficulty with such a procedure is to bring the pressure *continuously* on the plate. If the pressing weight meets the plate with some impulse then the pressure is much higher at first and will gradually (eventually oscillating) come down to the amount of the weight. Accordingly the changes in potential will also be too high at first and afterwards diminish. It will be very difficult to distinguish this decrease of potential from the natural electrostatic leakage. I have tried to avoid this difficulty in the following manner: The pressing weight was a cylindrical vessel attached to a frame work which pressed with a metal point on the upper copperplate in the box *B*. This vessel, when no weight was pressing, floated in a basin with water standing on a disk which could be moved upwards and downwards. Moving the disk continuously downwards the pressure was brought nearly continuously on the crystal.

The string electrometer of the WULF type was kindly put at the disposal of the laboratory by Professor D. VAN GULIK at Wageningen. This electrometer was put in a metal box to prevent electrostatic induction. This metal box as well as the frame of the electrometer itself were connected to earth. With the aid of a storage battery the one field plate was put at  $+80$  Volts, the other at  $-80$  Volts. The string was a platinum wire of 0.002 mm thickness. In the ordinary manner the field plates were placed symmetrically with regard to the string. The sensitivity of the electrometer was such that one part of the scale corresponded to about 0.05 Volt.

Before and after a series of measurements, which took place in about an hour, the scale of the electrometer was empirically calibrated in Volts. One measurement of the piezo-electric modulus consists of the following manipulations:

1. The electrometer string connected to the one side of the crystal is connected to earth and then insulated. If the string, when insulated, gets spontaneously an increasing deviation, this is a proof that the crystal or the copperplates are not sufficiently cleaned. (The deviation is caused by an electric polarisation).

2. The pressure is put on the crystal by moving the water basin downwards, and the deviation is read. Afterwards the natural leakage is determined. In most cases, when the room was sufficiently heated to avoid moisture this leakage was so small that no correction had to be made for it.

3. The electrometer is again connected to earth and then insulated.

4. By moving the water basin upwards the pressure is taken away, the electrometer gets a deviation in the opposite direction, which is read.

The deviations read in case 2 and 4 were sensibly the same, as can be seen from table 1. As an example in this table the deviations are given for crystal II negative (See also table 2).



TABLE 1.  
Deviations of the electrometer in volts.

Pressure on	Pressure off
1.280	1.275
1.265	1.275
1.285	1.275
1.225	1.250
1.250	1.260
1.285	1.270

Besides, in order to eliminate the unknown capacity of the system, the same four manipulations were repeated when an additional capacity of known magnitude was connected to it. If the deviation first is  $V_1$  (measured in units of tension) and after the capacity of magnitude  $C$  was connected to the system  $V_2$ , then it is easily seen that the charge set free is:

$$e = \frac{C}{\frac{1}{V_2} - \frac{1}{V_1}}$$

If the pressing weight is  $G$ , then the charge set free per unit of force is:

$$k = \frac{1}{G} \frac{C}{\frac{1}{V_2} - \frac{1}{V_1}}$$

§ 3. The zincblende crystals used were the crystals called I and II in our former work<sup>1)</sup>, cut by STEEG and REUTER parallel to the 111-planes. They have a surface of about 2 cm<sup>2</sup> and are about 3 mm thick. They gave good X-ray reflection on their whole surface so that we may assume that the formation of twins, such a common phenomenon with polar crystals and especially with zincblende, in these cases does not play an important part. The pressing weight was 1632 grams. The capacity of known magnitude was a condensor of HARMS<sup>2)</sup>, made by GÜNTHER and TEGETMAYER. It was used for a capacity of 43.21 cm. The values obtained are inserted in Table 2, they are given as charge in electrostatic c.g.s. units per kg pressure. For each crystal two sets of measurements were made, one set of measurements when the electrometer is getting a *positive* charge by putting the pressure on (1<sup>st</sup> and 3<sup>d</sup> column of table 2) the other with

<sup>1)</sup> l. c.

<sup>2)</sup> F. HARMS, Physik. Zs. 5, 47, 1904.



TABLE 2.

Charge set free in electrostatic c. g. s. units per kg pressure.

Crystal I		Crystal II	
Positive	Negative	Positive	Negative
0.0553	0.0547	0.0538	0.0575
0.0538	0.0569	0.0535	0.0573
0.0533	0.0572	0.0537	0.0555
0.0540	0.0556	0.0548	0.0553
0.0532	0.0568	0.0534	0.0555
0.0535	0.0565	0.0541	0.0542
0.0539	0.0570		
0.0545	0.0553		
0.0545	0.0564		
	0.0560		
Mean value	0.0540	0.0539	0.0559

the crystal inverted when it gets a *negative* charge in the same way (2<sup>d</sup> and 4<sup>th</sup> column of table 2). The mean of all the values obtained is 0.0550 electrostatic units per kg.

The agreement between the different values is sufficiently good. It is a curious fact that for both crystals the first set gives a mean value nearly 4 per cent smaller than the second set. This cannot be due to an asymmetry of the electrometer deviation because for both sets (compare § 2) deviations of the electrometer to the left as well as to the right were used. For the moment we cannot explain this small discrepancy.

As this discrepancy-though it is a rather small one- as long as its cause is not understood, gives an uncertainty as to the reliability of the results, we thought it desirable to have a control by measuring with the same apparatus a piezo-electric constant which is already well known. Now the best known piezo-electric constant is undoubtedly the modulus  $\delta_{11}$  of quartz which has been measured repeatedly by such skilled experimenters as CURIE and RÖNTGEN. It is a happy circumstance, indeed, that the values they finally obtained converged to nearly the same number: CURIE<sup>1)</sup> found  $\delta_{11}=0.0677$  (per kg), whereas RÖNTGEN<sup>2)</sup> got  $\delta_{11}=0.0681$  (per kg).

We used for our measurements with quartz a commercial piezo-quartz

1) J. P. CURIE, See Mme CURIE, *Traité de radioactivité*, Paris 1910.

2) W. C. RÖNTGEN, *Ann. d. Phys.* **41**, 449, 1913.

crystal as they are used for tuning high frequency oscillation circuits<sup>1)</sup>. The crystal had a surface of  $1.3 \times 2.8 \text{ cm}^2$  and was 1.5 mm thick. It was cut perpendicularly to the electric axis. If compressed in this direction a charge comes free

$$e = \delta_{11} P$$

where  $P$  is the force applied in the direction of the electric axis and  $\delta_{11}$  is the piezo-electric modulus when the axes of reference are properly chosen.

The crystal was highly polished on both surfaces; these were coated with a thin layer of copper. The values obtained in the same way as described in the case of zincblende are inserted in table 3. We find for the modulus  $\delta_{11}$  of quartz in the mean 0.0671 electrostatic units per kg pres-

TABLE 3.  
Piezo-electric modulus  $\delta_{11}$  of quartz in  
electrostatic c.g.s. units per kg pressure

Positive	Negative
0.0654	0.0697
0.0646	0.0680
0.0634	0.0684
0.0664	0.0672
0.0682	0.0668
0.0690	0.0667
0.0662	0.0677
0.0666	0.0676
0.0666	0.0680
0.0663	0.0678

sure, which is only 1 per cent less than the mean value of CURIE and RÖNTGEN. If this difference should be due to some systematic error in our apparatus (e.g. too small a value assumed for the known capacity), then we had to correct our value for zincblende with 1 per cent and we thus find for the constant  $k$  defined in § 2:

$$k = 0,0555 \text{ electrostatic c. g. s. units per kg.}$$

§ 4. As has been mentioned in § 1 we succeeded formerly<sup>2)</sup> in determining the piezo-electric effect of zincblende in a qualitative way. A

<sup>1)</sup> Supplied by STEEG and REUTER, Homburg v. d. Höhe, Germany.

<sup>2)</sup> l. c.

summary of the results seems justified here. Zincblende belongs to the cubic system, the 111-planes are alternately occupied by zinc- or by sulphur-atoms. The sulphur planes divide the distance between the successive zinc planes in the ratio 1:3. Now there is a difference in intensity of reflection for X-rays for the two different 111-planes *A* and *B* (see figure 2), which shows some anomalies in the neighbourhood of the absorption edge of zinc. This afforded a means to make sure which of the 111-planes

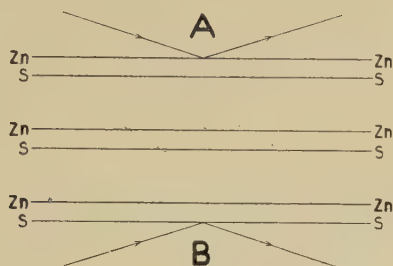


Fig. 2. Reflection of X-rays on the both 111-planes *A* and *B* of zincblende.

of the crystals I and II has to be identified with *A* (figure 2) and which with *B*. A piezo-electric determination showed at the same time, that if the crystal is compressed in a direction perpendicular to the 111-planes (i.e. in the direction *A—B* of figure 2), then the plane *A* gets a negative and the plane *B* a positive charge. As mentioned above, this charge is:

$$k = 0,0555 \text{ electrostatic c. g. s. units per kg.}$$

Now the question arises how we have to derive the piezo-electric modulus of zincblende from the value of *k*. The piezo-electric constants and moduli have to be referred to the common crystal axes i.e. the cubic axes in the regular system. VOIGT<sup>1)</sup> has shown that from the 18 piezo-electric constants in the case of the regular system only 3 may be different from zero. The same is true for the moduli. These moduli have the following meaning

$$-p_x = \delta_{14} Y_z$$

$$-p_y = \delta_{25} Z_x$$

$$-p_z = \delta_{36} X_y$$

Here  $p_x$ ,  $p_y$  and  $p_z$  are the components of the electric polarisation caused by the components of shearing stress  $Y_z$ ,  $Z_x$  and  $X_y$ . For cubic crystals these moduli are equal to one another, usually they are all denoted by  $\delta_{14}$ . The connection between  $\delta_{14}$  and the constant *k* determined in § 3 is easily seen with the help of figure 3.

The angle which the 111-plane makes with the three coordinate planes is

$$\arccos \frac{1}{3} \sqrt{3}.$$

<sup>1)</sup> W. VOIGT, *Lehrbuch der Kristallphysik*, Leipzig 1928.

If a crystal is compressed by a pressure  $D$  perpendicular to the 111-plane, the resultant stress on the  $Oyz$ -plane has the direction of  $D$  and the

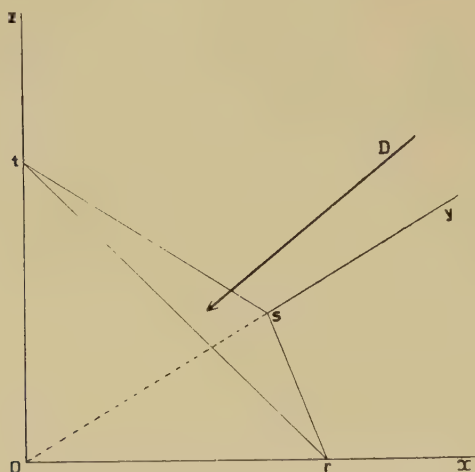


Fig. 3. 111-plane ( $r s t$ ) and the 3 cubic planes ( $Oxy, Oyz, Ozx$ ).

magnitude  $\frac{D}{\sqrt{3}}$ . This resultant stress has as components along the axes: the pressure  $X_x$  and the shearing stresses  $Y_x$  and  $Z_x$ . Every component is  $\frac{1}{3}\sqrt{3} \cdot \frac{D}{\sqrt{3}} = \frac{D}{3}$ . Because of the symmetry of the problem we must assume that the 3 shearing stresses which are of interest,  $Y_z$ ,  $Z_x$  and  $X_y$  are each  $\frac{D}{3}$ . The polarisation they give has equal components along the axes

$$p_x = -\delta_{14} \frac{D}{3}.$$

Therefore the resultant polarisation  $p = \sqrt{3} p_x = -\delta_{14} \frac{D}{\sqrt{3}}$ . We thus see that the constant  $k$  measured in § 3  $= \frac{\delta_{14}}{\sqrt{3}}$ . We find in this manner for the modulus  $\delta_{14}$  in c.g.s. units

$$\delta_{14} = \frac{\sqrt{3}}{9,81 \cdot 10^5} k = 9,80 \cdot 10^{-8}$$

In conclusion I wish to express my sincere thanks to Prof. Dr. D. COSTER for his kind interest and his many valuable suggestions and to Mr. H. BULTHUIS and Mr. C. SCHOLTENS for their assistance in the performance of the measurements.

*Natuurkundig Laboratorium der Rijks-Universiteit  
te Groningen.*

**Chemistry.** — *Die numerische Festlegung der lyotropen Reihe.* Von E. M. BRUINS. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of January 30, 1932.)

1. Den Ausgangspunkt der nachstehenden Betrachtungen bilden die Untersuchungen, welche Dr. E. H. BÜCHNER und D. KLEYN<sup>1)</sup> sowie erstgenannter und G. POSTMA<sup>2)</sup> über das Aussalzen von Solen durch Salzmischungen anstellten.

Die aus beiden Untersuchungen in den Abhandlungen gezogenen Schlüsse stimmen in der Hauptsache überein. Sowohl bei Agarsolen als bei Gelatine tritt, wenigstens bei höherer Konzentration, eine völlige Ersetzbarkeit der flockenden Salze ein, was sich in den graphischen Darstellungen (siehe die entlehnten Figuren 1 und 2) in dem Auftreten gerader Linien äussert. Die zu verschiedenen Salzen gehörenden Linien breiten sich fächerförmig aus.

Anfangs wurden nun, auf Grund von Untersuchungen, die BÜCHNER und KLEYN an Agarsolen angestellt hatten, die Salze in zwei Gruppen, die flockende und die antiflockende Gruppe, verteilt.

Aus den von BÜCHNER und POSTMA mit Gelatinesolen erhaltenen Resultaten ergab sich, dass die Reihenfolge der geraden Linien im Fächer sowohl für Agar als für Gelatine dieselbe blieb, dass jedoch die Trennung der Salze in die beiden vorgenannten Gruppen ein völlig anderes Ergebnis zeitigte. BÜCHNER und POSTMA folgerten damals, dass offenbar der Übergang nach einem anderen Kolloid den Übergang einiger Salze von der flockenden nach der antiflockenden Gruppe oder umgekehrt zur Folge haben könne.

Die nachstehenden Betrachtungen bezwecken nun, den Nachweis zu erbringen, dass wahrscheinlich eine Gesetzmässigkeit in diesem Übergang eines Salzes von der flockenden nach der antiflockenden Gruppe besteht und dass sich die Möglichkeit darbietet, die lyotrope Reihe statt durch Grösser- und Kleiner-Relationen numerisch festzulegen.

2. Man denke sich, dass ein Flockungsdiagramm, wie dies in den oben zitierten Abhandlungen (Fig. 1 und 2) vorkommt, für Salzmischungen aufgestellt wird, die weder Synergismus noch Antagonismus<sup>3)</sup> der

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1) Diese Proceedings 30, S. 740, 1927.

2) Diese Proceedings 34, S. 699, 1931.

3) Unter Synergismus (Antagonismus) der Ionen wird hier die Erscheinung verstanden, dass man, um den Flockungswert einer Salzmischung zu erreichen, bei einer bestimmten Konzentration des einen Salzes von dem anderen Salz eine kleinere (grössere) Konzentration benötigt, als sich aus einer gegenseitigen Ersetzbarkeit der Salze ergibt.



Ionen zeigen. In diesem Falle werden sich die Salze vollkommen additiv verhalten und wird das Diagramm einen aus Geraden bestehenden Fächer aufweisen (siehe Fig. 3).

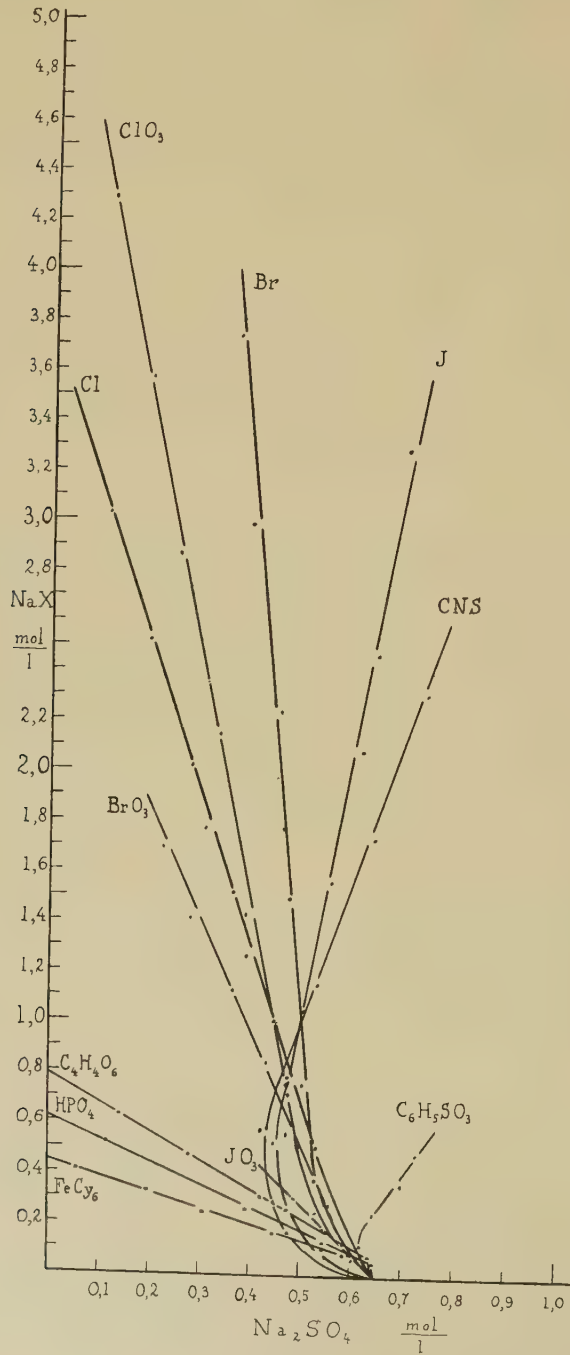


Fig. 1.

In der Tangente des Winkels  $\varphi$ , den eine der Linien mit der Horizontalachse bildet, hat man dann das Verhältniß der Flockungswerte der beiden Salze, wodurch diese Flockungslinie bestimmt wird.

Nimmt man nun weiter einen Punkt  $P$  auf der Flockungslinie der Mischung  $Na_pX - Na_qY$ , dann wird in diesem Punkt  $P$  die Konzentration der  $Na^+$ -Ionen der flockenden Mischung  $pa + qb$  sein.

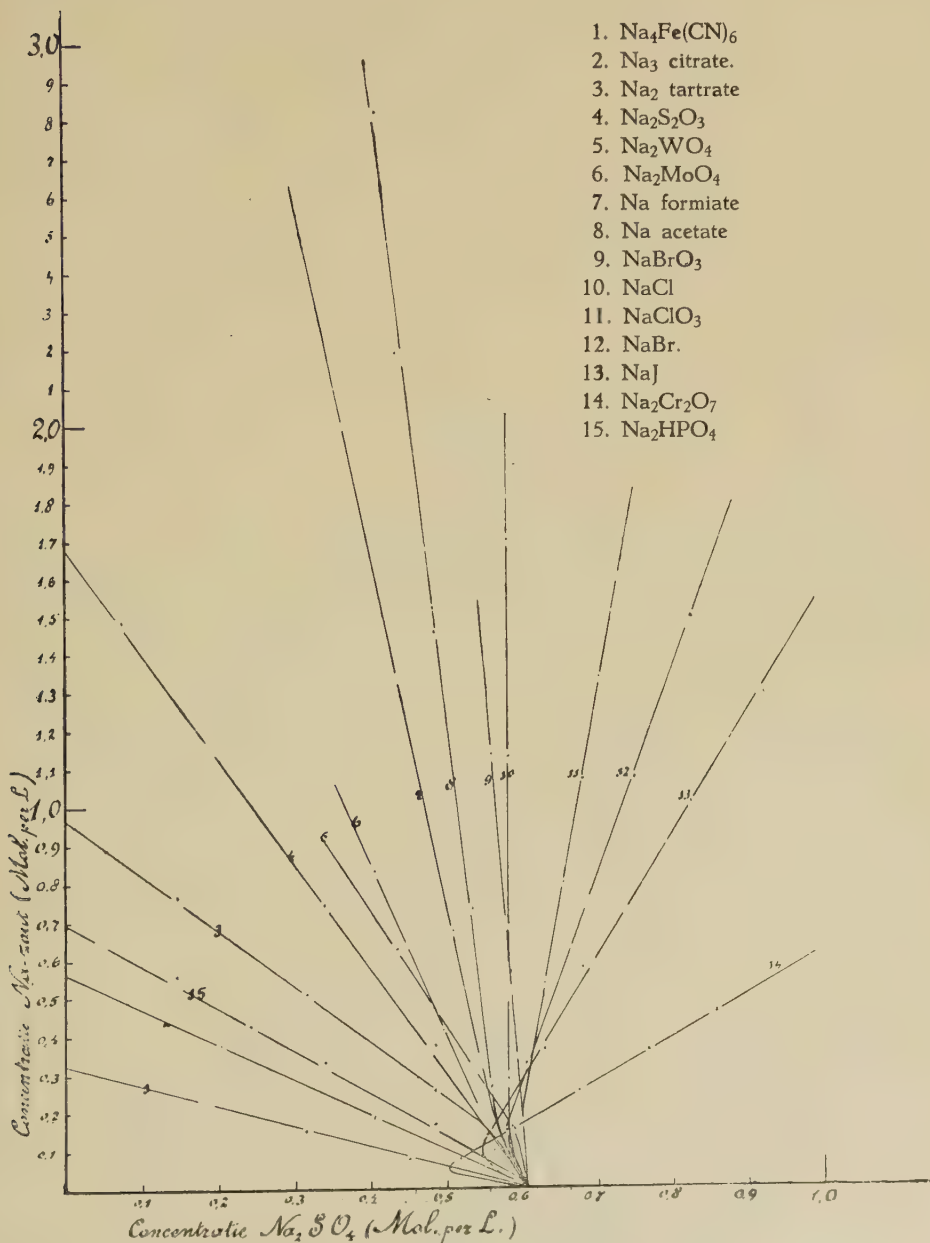
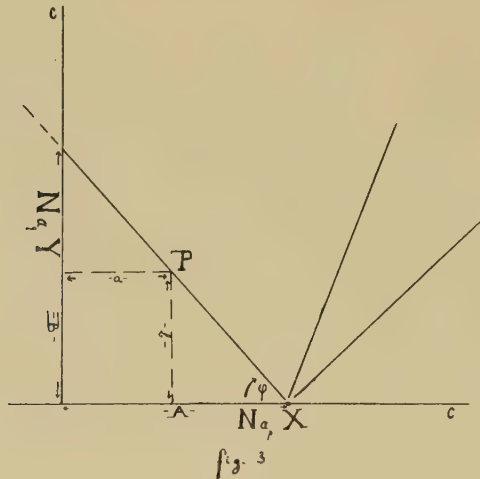


Fig. 2.

Die Konzentrationen der Anionen  $X^-$  und  $Y^-$  genügen der linearen Gleichung:

$$\frac{[X^-]}{A} + \frac{[Y^-]}{B} = 1$$

Verschiedene Punkte  $P$  auf der Flockungslinie ergeben verschiedene Konzentrationen der  $Na^+$ ,  $X^-$  und  $Y^-$  Ionen. Nimmt man den Punkt  $P$



in dem unendlich fernen Punkt der Geraden, so werden in der gerade flockenden Mischung die Konzentrationen aller Ionen unendlich gross; das Verhältnis zwischen den Konzentrationen der Anionen aber wird eine bestimmte Zahl, nämlich  $-\tan \varphi$ .

3. Tritt anfänglich wohl ein Zusammen- oder Entgegenwirken der Ionen ein, dann ergibt die Tangente des Winkels, den der gerade Teil der Flockungslinie mit der Horizontalachse bildet, nicht direkt einen Flockungswert. Man kann diese Grösse ( $\tan \varphi$ ) jedoch wohl als ein Mass für das flockende oder antiflockende Vermögen der Anionen auffassen.

Nun ergibt ein bestimmtes beigemischtes Salz in jedem Flockungsdiagramm eine bestimmte Kurve, und damit, bei höheren Konzentrationen, eine bestimmte  $\tan \varphi$ .

In zwei derartigen Diagrammen, z.B. demjenigen BÜCHNER und KLEYN's und dem Diagramm von BÜCHNER und POSTMA, stehen dann die Richtungskonstanten ( $\tan \varphi$ ) in einer ein-eindeutigen Verwandtschaft. Nehmen wir an, dass diese Verwandtschaft algebraisch ist, dann besteht zwischen den  $\tan \varphi$  der Kurven von BÜCHNER und KLEYN ( $x$ ) und denjenigen von BÜCHNER und POSTMA ( $y$ ) eine Gleichung von folgender Gestalt:

$$xy + Ax + By + C = 0,$$

in welcher  $A$ ,  $B$  und  $C$  Konstanten sind.

Deutet man  $x$  und  $y$  als rechtwinklige Koordinaten, dann wird, falls die

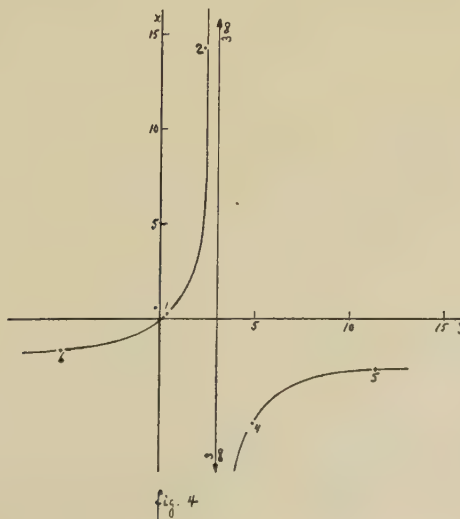
Annahme einer algebraischen Verwandtschaft richtig ist, eine Hyperbel mit der  $x$ - und  $y$ -Achse als asymptotische Richtungen zum Vorschein kommen.

Die Winkel wurden für die anorganischen neutralen Salze gemessen, die in beiden Diagrammen vorkommen. Die Resultate hiervon sind in der nachstehenden Tabelle I und graphisch in Figur 4 niedergelegt.

TABELLE I.

		Gelatine			Agar		
No.	Salz	$\varphi$	$\text{tang } \varphi$	$\text{cotg } \varphi$	$\varphi$	$\text{tang } \varphi$	$\text{cotg } \varphi$
1	$\text{Na}_4\text{FeCy}_6$	$17^\circ$	0.306	3.27	$15^\circ$	0.267	3.73
2	$\text{NaBrO}_3$	$65.5^\circ$	2.19	0.456	$86^\circ$	14.30	0.069
3	$\text{NaCl}$	$72^\circ$	3.08	0.325	$90^\circ$	$\infty$	0
4	$\text{NaClO}_3$	$78.5^\circ$	4.92	0.203	$100.5^\circ$	-5.40	-0.185
5	$\text{NaBr}$	$85^\circ$	11.43	0.087	$110.5^\circ$	-2.67	-0.374
6	$\text{NaI}$	$101^\circ$	-5.14	-0.194	$122^\circ$	-1.60	-0.625

Jedem Punkt im  $x$ - $y$ -Diagramm (Fig. 4) ist die Nummer gegeben, die in vorstehender Tabelle dem beigemischten Salz zukommt. Durchläuft man dann die Fächer der geraden Stücke in den Flockungsdiagrammen von Salz No. 1 bis Salz No. 6, dann beschreibt der Punkt ( $x$ ,  $y$ ) eine Kurve.



die gerade so durchlaufen wird, wie dies bei der betreffenden gleichseitigen Hyperbel geschieht.

4. Von dieser Hyperbel kann man an Hand einiger besonderer Bemerkungen noch ein paar Punkte finden.

a. Man denke sich ein Salz  $NaZ$  bestehe mit einer unendlich grossen flockenden (oder peptisierenden) Wirkung. In diesen Fällen — die Extreme berühren sich — fällt die Flockungslinie mit der negativen (bezw. positiven) Sulfatachse zusammen. Diese Kurven entsprechen einander ebenfalls in der Verwandtschaft. Die  $\tan \varphi$  ist Null für beide extreme Fälle (und in *allen* für flockende Mischungen aufgestellten Diagramme).

Die Hyperbel  $xy + Ax + By + C = 0$  muss also durch den Punkt (0.0) gehen, d.h. die Konstante  $C = 0$ .

In der Gleichung bleiben somit noch zwei Konstanten übrig.

b. Dass zwischen diesen letzten zwei Konstanten noch eine Beziehung besteht, erhellt aus Folgendem:

Hätte man auch unter die beigemischten Salze das Sulfat (und im allgemeinen das „Basissalz“ für das Diagramm) gewählt, dann würde die hierfür aufgestellte Flockungslinie eine Gerade sein. In beiden Diagrammen, sowohl demjenigen von BÜCHNER und KLEYN als dem von BÜCHNER und POSTMA würde, da die Längeneinheit auf der Achse der beigemischten Salze genau die Hälfte derjenigen auf der Sulfatachse ist, für das Sulfat eine  $\tan \varphi = \frac{1}{2}$  gefunden werden.

Die Hyperbel muss mithin auch durch den Punkt  $(\frac{1}{2}, \frac{1}{2})$  gehen, und zwischen dem  $A$  und dem  $B$  besteht daher die Beziehung:

$$A + B + \frac{1}{2} = 0.$$

In der Gleichung der Hyperbel kommt demnach nur noch *eine* beliebige Konstante vor.

## 5. Aus den Beziehungen

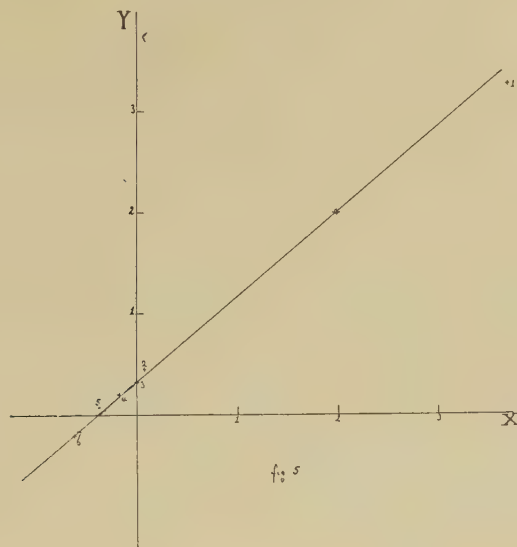
$$\left. \begin{aligned} xy + Ax + By &= 0 \\ A + B + \frac{1}{2} &= 0 \end{aligned} \right\}$$

für die Tangenten  $x$  und  $y$  folgt, dass, wenn man die Kotangenten  $X$  und  $Y$  statt der Tangenten  $x$  und  $y$  als Koordinaten deutet, man eine Gerade durch den Punkt (2.2) erhalten wird. Dies ist in Figur 5 ausgeführt. Dort ist die durch den Punkt (2.2) gehende Gerade gezeichnet bei der die Summe der Quadrate der Abstände der Punkte minimal ist. Man findet leicht als Gleichung dieser Geraden:

$$(Y - 2) = 0,813(X - 2)$$



worin  $Y$  und  $X$  die laufenden Koordinaten sind. Abweichungen von der Geraden, die etwa auftreten, sind experimentell als zulässig zu bezeichnen.



6. Durch Vergleichen des Fächers aus Fig. 1 mit demjenigen aus Fig. 2 gelangt man also zu dem Ergebnis, dass die Richtungen der geraden Stücke projektiv einander zugefügt sind. Ausserdem liefern das imaginäre Salz mit unendlich flockender Wirkung und das imaginäre Mischen einer Salzlösung mit sich selbst — wie dies oben abgeleitet wurde — zwei Gleichungen zwischen den Koeffizienten der Gleichung:

$$xy + Ax + By + C = 0,$$

— die die Projektivität definiert — nämlich

$$C = 0 \quad \text{und} \quad A + B + \frac{1}{2} = 0.$$

Bestimmt man nun noch die  $\tan \varphi$  für eine *wirkliche Mischung*, in beiden Diagrammen, dann kann man  $A$  und  $B$  berechnen und mit Hilfe hiervon, aus der Richtung der Flockungslinie eines Salzes bei der Agarsole diejenige desselben Salzes für Gelatine berechnen, und umgekehrt.

7. Gesetzt, man erkenne jedem Salz  $KA$  eine „lyotrope Zahl“ zu, die gleich der  $\cotg \varphi$  des geraden Stücks der Flockungslinie ist. Nach dem Vorangehenden sind dann die Zahlenreihen, die aus einer Gruppe Salze

$$KA_1, KA_2, KA_3 \dots KA_r,$$

dadurch entstehen, dass jedem Salz die  $\cotg \varphi$  aus einem bestimmten Flockungsdiagramm zuerkannt wird, projektiv gleichwertig, d.h.: die

Zahlen  $N$  und  $M$  aus zwei derart aufgestellten Zahlenreihen genügen einer Beziehung:

$$N = \frac{aM + 1}{bM + c},$$

worin  $a$ ,  $b$  und  $c$  Konstanten sind.

Man kann dann eine Reihe von „absoluten lyotropen Zahlen  $N$ “ aufstellen und zwar folgendermassen:

Man weist drei Anionen,  $A_1$ ,  $A_2$  und  $A_3$  die Zahlen  $N_1$ ,  $N_2$  und  $N_3$  zu. Aus einem Flockungsdiagramm findet man die hierzu gehörende  $\cotg \varphi$ , bezw.  $M_1$ ,  $M_2$  und  $M_3$ . Aus diesen drei Data sind  $a$ ,  $b$  und  $c$  zu berechnen, und durch die  $\cotg \varphi = M$  ist dann für ein beliebiges weiteres Anion  $A$  die absolute lyotrope Zahl  $N$  bestimmt.

8. Nach den in diesem letzten Abschnitt (7) erhaltenen theoretischen Resultaten kann man somit aus einem einzigen Flockungsdiagramm eine Reihe „absoluter lyotroper Zahlen“ herleiten.

Ordnet man nun dem imaginären Salz mit einer unendlich flockenden (oder peptisierenden) Wirkung — aus mathematischen Erwägungen — ein  $N = \infty$  zu, dann wird in der oben zitierten Formel:

$$N = \frac{a \cdot \cotg \varphi + 1}{b \cdot \cotg \varphi + c}$$

das  $b$  Null werden müssen.

Ein  $N$ - $\cotg \varphi$ -Diagramm wird dann *immer eine Gerade* aufweisen statt einer gleichseitigen Hyperbel.

Zur weiteren Ausarbeitung setzt man z.B. das  $N$  des  $\text{SO}_4$ -Ions  $= 2.00$  und dasjenige des  $\text{Cl}$ -Ions  $= 10.00$ ; (beides ganz beliebige Grössen).

Man kann dann die Gleichung der betreffenden Geraden aus dem Diagramm BÜCHNER's und KLEYN's berechnen und findet hierfür:

$$N = -4.00 \cotg \varphi + 10.00$$

und aus den Data des Diagramms von BÜCHNER und POSTMA:

$$N = -4.78 \cotg \varphi + 11.55$$

Für die weiteren Ionen findet man die Ziffern in Tabelle II festgelegt.

TABELLE II.

	FeCy <sub>6</sub>	BrO <sub>3</sub>	ClO <sub>3</sub>	Br	I	
BÜCHNER und KLEYN	-4.92	+9.72	10.74	11.50	12.50	Agar
BÜCHNER und POSTMA	-4.08	+9.38	10.58	11.14	12.48	Gelatine

Somit ist eine numerische Festlegung der lyotropen Reihe erreicht.

9. Nunmehr liegen auch einige chemische Folgerungen auf der Hand,

a. betreffs der Zahl  $N$  für die Anionen.

Sowohl der absolute Wert als das Zeichen der Ziffern in Tabelle II sind unwesentlich; man kann drei beliebig zu wählenden Anionen drei beliebige Zahlen zuweisen. Wesentlich ist, dass jedem der übrigen Anionen dann eine eindeutige bestimmte Zahl  $N$  zukommt.

Bisher hat man die lyotrope Reihe immer mit dem „wasserbindenden Vermögen“ ( $H$ ) der Ionen in Zusammenhang gebracht.

Man könnte mithin weiter erwarten, dass

$$N = f(H).$$

Es ist zweifelhaft, ob aus demjenigen, was bezüglich dieses wasserbindenden Vermögens bekannt ist, sich jetzt schon ein Bestehen bzw. Nichtbestehen einer derartigen Beziehung nachweisen lässt.

b. betreffs der hydrophilen Solen.

Sowohl für die Agar- als für die Gelatinesole ist eine Beziehung folgender Gestalt:

$$N = A \cdot \cotg \varphi + B$$

nachgewiesen.

Das  $N$ - $\cotg \varphi$ -Diagramm ergibt also für beide — und wahrscheinlich für alle — hydrophile Solen eine Gerade.

Durch die Wahl des Basissalzes und der Längeneinheiten auf den Achsen des Flockungsdiagramms wird ein Punkt dieser Geraden festgelegt. Bei der Gelatine und dem Agar war dieser Punkt  $N=2$ ,  $\cotg \varphi=2$ .

Die Agarsole und die Gelatinesole unterscheiden sich also in ihrem Verhalten gegenüber der *lyotropen Reihe als Ganzes*. Dieser Unterschied kommt zum Ausdruck in einem verschiedenen Wert einer einzigen Konstante, die mathematisch durch die Richtung der Geraden aus dem  $N$ - $\cotg \varphi$ -Diagramm durch den Punkt (2.2) festgehalten wird.

Da das  $p_H$  der Gelatine immer nahezu konstant war, wird ein Einfluss der Ladung der Mizellen in den Flockungswerten gewiss nicht in den Vordergrund treten. Es liegt somit, in Zusammenhang mit der heutigen kolloid-chemischen Theorie, nahe, dass sich hier die verschiedene Hydratation der Mizellen äussert.

Es ist dem Verfasser ein Bedürfnis, seinem Lehrer, Herrn Dr. BÜCHNER (Amsterdam) an dieser Stelle seinen warmen Dank für die erteilten Ratschläge bei der Bearbeitung dieses Problems auszusprechen.

Amsterdam. Anorganisch chemisches  
Laboratorium der Universität.

**Bacteriology.** — *Further Observations on the Bacteriophage of Bacillus megatherium.* By L. E. DEN DOOREN DE JONG. (Communicated by Prof. A. J. KLUYVER).

(Communicated at the meeting of January 30, 1932.)

When I last wrote about the bacteriophage of *Bac. megatherium*<sup>1)</sup> I took for granted that when the spores of *Bac. megatherium* were heated to temperatures destructive to the bacteriophage in vitro (e.g. 10' at 90° C), the spores would be rid of a possibly existing bacteriophage infection. Hence when it was found that the cultures of certain strains of *megatherium*, after being subjected to a careful pasteurization for 10' or 15' at 90° C or 100° C, and then filtrated, still contained a very active bacteriophage for certain *megatherium* mutilates, this fact was looked upon as an absolute proof of the bacteriophage not being an autonomic ultra microbe, but a product of the living bacterial cell.

Several investigators in our country<sup>2)</sup> and also COWLES<sup>3)</sup> have fully confirmed the correctness of the above mentioned experiments. They suggested the possibility of the spores transmitting their thermoresistant properties to foreign substances which they had included at the time of their spore formation, as an explanation of the phenomena. Hence according to them the phage in the bac. spore would pass into another unknown but more resistant form, since from a physical point of view it is not thinkable that during the process of pasteurization a temperature lower than the surrounding one could be maintained inside the spore. Although there are various objections to this hypothesis, still the fact that so little is known of the factors determining the thermoresistance of the spores, makes it desirable for us to test its value by further experiments.

Firstly experiments were done to find out whether strains of spore forming bacteria which had never been found to possess the property of phage production, could be brought to do so by allowing the bacteriophage to act upon them during the process of spore formation. The positive result of these experiments which were begun in the middle of 1930, does not necessitate our accepting D'HERELLE's theory of the

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<sup>1)</sup> The bacteriophage of *Bac. megatherium*; a product of the living bacterial cell. Proceedings Kon. Akad. v. Wetensch. **33**, N<sup>o</sup>. 1 (1930), 51 and Ned. Tijdschr. v. Hyg. Microb. en Serol. **4**, 255 (1930); Studien über Bacteriophagie I Zbl. Bakter. I, Orig. **120** p.l. (1931).

<sup>2)</sup> See on this subject Ned. Tijdschr. v. Hyg. Microb. en Serol. **5**, 54 (1931) and C. R. RITSEMA VAN ECK, diss. Leyden 1931.

<sup>3)</sup> PH. B. COWLES, J. Bact. **22**, 119 (1931).



autonomic ultramicrobial nature of the phage. After further consideration it seemed quite possible to find an explanation of the phenomena in a further development of my view of the subject. It seems to me quite reasonable to think of the phage which has been brought into the bacteria cell, as only acting as a stimulus to the latent power of phage formation in that cell. In other words the phage found after the process had taken place, would owe its origin to the bacteria cell itself, and not at all to the phage, which had provided the stimulus to phage formation. In the meantime COWLES' article mentioned above appeared in August 1931. He too came to the conclusion that non-bacteriophagic strains of several spore forming micro-organisms (*Bac. megatherium*, *Cl. tertium* and more especially *Bac. anthracis* and *Bac. subtilis*) could be acted upon by diverse homologous bacteriophages and altered in such a way that the lytical principle could be demonstrated in filtrates of cultures which had been obtained from heated spores. But his spores which we may look upon as artificially "infected" were never infected to such a degree as the spores of the *megatherium* strains which I had used and which following my line of thought might be looked upon as naturally infected. All the colonies of these cultures contrary to the artificially infected *subtilis* strain produced active filtrates and heating them up to temperatures which the spores could only just bear was never able to destroy their phage producing powers. On the other hand pasteurization of the artificially infected *anthracis* strains up to 95° C. was able to destroy the phage producing powers of those cultures. COWLES came to the following conclusion: "This does not necessarily mean that the lytic agent as such survives the heating process but it does mean that the recovering of a lytic principle from a pasteurized culture is not conclusive proof of the spontaneous generation of bacteriophage".

The results of these experiments led me to take up a more elaborate study of the question of artificial "infection". I have not confined myself to the *Bac. megatherium* as I did in the past, but have used other species of the genus *Bacillus*. Unlike COWLES I always confined myself to the use of *megatherium* bacteriophages, first taking the phage of *megatherium* N<sup>o</sup>. 899 and using the two types 899 O and 899 ⊙. A dissemination of filtrates of *Bac. megatherium* 899 like those of 333, on spreadings of almost all of the susceptible *megatherium* mutilates, gave rise to two kinds of plaques, the normal round hole form of plaque, and a second form with a small bacteria colony in the centre (called dot plaques). If the culture is allowed to go on incubating<sup>1)</sup>, a concentric ring of bacteria material is formed. As far as we could see the two types of 899 never interchanged. Hence it seemed to me important, moreover, to find out whether both types of phage only led to the production of its own type when used to activate the spores of phage free strains.

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<sup>1)</sup> Zbl. Bakter. 1 Orig. 120 p. 19 (1931).



### A. Experiments with the 899 O phage.

This phage was obtained by putting strain 899 in an ERLÉNMEYER bulb with 1 % peptone water and incubating for two days at 30° C., after which the culture was filtered through a Seitz filter. The filtrate obtained was disseminated in various degrees of dilution from  $10^{-1}$  to  $10^{-6}$  c.c. on spreadings of a specially susceptible *megatherium* mutilate viz. 338b' <sup>1)</sup>. The plates obtained were then incubated at 37° C. Within 24 hours they showed a mixture of two kinds of plaques which when obtained from the weaker solutions (usually  $10^{-5}$  or  $10^{-6}$ ) were situated so far from each other that they could be pricked away with the agar on which they were lying, without the danger of mutually infecting each other.

Then we took a bit of agar with an O plaque on it, and containing of course a little bacteria material necessary to increase the lytic principle, and inoculated it in 1 % peptone water and incubated for two days at 30° C. The culture fluid obtained was again filtered through a SEITZ filter. Its purity and concentration was tested and determined by disseminating the filtrate in varying degrees of dilution on 338b' spreadings. In the greater number of cases the filtrate so obtained was found to contain the pure phage, that was in this case 899 O, which at a temperature of 37° C. in 338b' always formed plaques with an average diameter of 2 m.m. It was sometimes necessary to repeat the process as one always ran the risk in digging out a large plaque, of taking a small undeveloped plaque of the other species with it.

We used the same strains for these experiments that we used in our previous research work on this subject, viz. *Bac. megatherium* 333, 334, 335, 336, 337, and 338. With the exception of 333 these strains were known to lack the power of producing a perceptible bacteriophage.

These six strains were inoculated in duplo on slanting 1 % peptone agar in tubes which were then put straight away into an incubator at a temperature of 37° C. Six hours later a thin transparent layer of bacteria could be seen on the peptonagar in all the tubes. Microscopic examination showed that no spore formation had taken place among the various spore forming bacteria. After that one of the two series of tubes was put in an incubator at 30° C. so as to facilitate spore formation. Then the other series of cultures was taken and 0.3 c.c. of the filtrate 899 O (able to produce per c.c.  $20 \times 10^7$  plaques in spreadings of 338b' when titrated), was added to each of the six tubes. Care was taken to cover the whole of the bacterial culture with the fluid. This series of cultures was then incubated at 30° C. The next day the bacterial layer in most of the tubes was found to be perceptibly more or less affected <sup>2)</sup>. Still after the lapse

<sup>1)</sup> For further details on this mutilate confr. Studien über Bakteriophagie II pp. 16 and 17.

<sup>2)</sup> I knew from former experiments that the spreadings of several *megatherium* strains e.g. 334, 335 and 337 if examined in very young sporeless condition, may form small plaques. (See Studien über Bakteriophagie II, note on page 15).

of a few days a considerable development of spore forming bacteria was found to have taken place in most cases, and these could be reasonably supposed to have been influenced by the phage.

A week after the filtrate had been added to the bacterial cultures, a fair amount of bacterial substance from each of the two series of tubes was inoculated in culture tubes containing 5 c.c. of peptone water. Then all the twelve inoculated tubes were pasteurized while entirely immersed in water for 10' at 90° C., as soon as possible after the inoculation had been carried out. Great care was taken to keep the temperature within the tubes at 90° C. during the 10'. Then they were cooled down quickly and placed in a temperature of 30° C., or 37° C., to give the bacteria the opportunity of multiplying, so as to facilitate their transference. Two days afterwards a little bacterial substance from each tube with the exception of 335 which had not survived the pasteurization, was inoculated into an ERLNMEYER flask containing 1 % peptone water. These cultures were incubated at 30° C. for two days and then filtrated. Then each of the 10 filtrates, five of which being filtrates of *megatherium* strains which had not been in contact with the 899 O and the other five having been in contact with the 899 O, was tested in various degrees of dilution on spreadings of the mutilate 338b'.

The filtrates derived from the strains which had not been treated with the phage 899 led to the following results:

Filtrate 333: When diluted  $10^{-3}$  thousands, when diluted  $10^{-5}$  hundreds of plaques averaging 0.5 m.m., belonging to the O and the ⊙ types.

Filtrate 334: When diluted  $10^{-1}$  no plaques.

Filtrate 336: " " " " " "

Filtrate 337: " " " " " "

Filtrate 338: " " " " " "

These results were absolutely in agreement with former observations.

The filtrates derived from strains which had been brought into contact with the 899 O phage before pasteurization, led to quite different results:

Filtrate 333: When diluted to  $10^{-1}$  only a few hundreds of plaques with an average diameter of 0.5 m.m. belonging to the O type and also to the ⊙ type<sup>1)</sup>. Plaques of 2 m.m. were not met with.

Filtrate 334: When diluted to  $10^{-1}$  a hundred plaques with a diameter averaging 2 m.m., all of the O type.

Filtrate 336: When diluted to  $10^{-2}$  a hundred plaques with an average diameter of 2 m.m., all of the O type.

<sup>1)</sup> It is noticeable that the 333 strain when treated with phage 899 always formed its own phage (plaques of 0.5 m.m.) and never a mixture of the two phages. Also that comparing it with the filtrate of the untreated strain, the titer of its own 333 phage had become less.

Filtrate 337: *When diluted to  $10^{-1}$  a hundred plaques with an average diameter of 2 m.m. all of the O type.*

Filtrate 338: *When diluted to  $10^{-1}$  no plaques.*

### *B. Experiments with the 899 ⊙ phage.*

We then made a pure culture of the phage 899 ⊙ in absolutely the same way as was done with the phage described under A. This too was found to lead to the formation of plaques on spreadings of 338b' and at 37° C., plaques with an average diameter of 2 m.m. The titer of the filtrate used had to be  $8 \times 10^7$ . The six *megatherium* strains were here too inoculated on slanting jellied 1 % peptone agar, incubated at 37° C., and then after six hours covered with 0.3 c.c. of the filtrate 899 ⊙. In some of the tubes the influence of the phage was noticeable, but still after the lapse of a week a considerable growth of the spore formers had taken place everywhere; then a fair amount of bacteria material was taken from each of the tubes and inoculated in tubes containing 5 c.c. 1 % peptone water. These suspensions were then pasteurized with the same precautions for 10' at 90° C., and then incubated at 30° C., or 37° C. Two days later a little bacteria material was taken from each tube with the exception of that containing 335, which in this case too had not survived the pasteurization, and inoculated in an ERLÉNMEYER bulb containing 1 % peptone water. These cultures were incubated for two days at 30° C., and then filtrated. The filtrates which were therefore derived from strains which had been treated with 899 ⊙ phage before pasteurization, led to the following results on the mutilate 338b':

Filtrate 333: *With a dilution of  $10^{-4}$  hundreds of plaques with a diameter averaging 0.5 m.m., belonging to the O and the ⊙ types; plaques with 2 m.m. were not found.*

Filtrate 334: *With a dilution of  $10^{-5}$  hundreds of plaques with a diameter averaging 2 m.m. all of the ⊙ type.*

Filtrate 336: *With a dilution of  $10^{-4}$  tens of plaques with a diameter averaging 2 m.m., the greater number belonging to the ⊙ type, and a few to the O type.*

Filtrate 337: *With a dilution of  $10^{-5}$  hundreds of ⊙ plaques with a diameter of 2 m.m. and a few O plaques with a diameter of 2.5 m.m.*

Filtrate 338: *With a dilution of  $10^{-1}$  no plaques.*

Hence from these experiments with the two pure 899 phages described under A and B, it seemed that the "inclusion" of these phages in the forming spores led to the presence of the lytic principle in the pasteurized spores. It is remarkable, however, that in a few cases (working with strain 336 and 337) the spores seemed able to transform the ⊙ phage into the O



phage, although only to a slight extent, a circumstance which, at any rate in the case of the 899 phage, has never been observed under normal conditions (without the intervention of living spores).

### C. *Experiments with the 333 O phage.*

A 333 filtrate was then made in exactly the same way as has been described under A, and then put on 338b' spreadings in various degrees of dilution. The O plaques were taken from the mixture and pure cultures were made from them. The 333 O filtrate thus obtained formed at 37° C. per c.c.  $36 \times 10^6$  plaques of 0.5 m.m. diameter on 338b' spreadings. And again in the same way as has been described above, 0.3 c.c. of this filtrate was poured on young still vegetative cultures of the *megatherium* strains 334, 336, 337, and 338, and a week later pasteurized for 10' at 90° C., and then inoculated in 1 % peptone water in an ERLNMEYER bulb. After being incubated for two days at 30° C. the cultures were filtrated and the filtrates obtained were tested on the mutilate 338b'. The following result was obtained :

Filtrate 334: With a dilution of  $10^{-1}$  no plaques.

Filtrate 336: With a dilution of  $10^{-1}$  no plaques.

Filtrate 337: *With a dilution of  $10^{-4}$  hundreds of plaques of the O type, of which by far the majority were 0.2 m.m. in diameter, and the rest 1 m.m. in diameter.*

Filtrate 338: *With a dilution of  $10^{-4}$  hundreds of plaques of the O type and 1 m.m. in diameter.*

### D. *Experiments with the 333 ⊙ phage.*

Then young vegetative cultures of the *megatherium* strains 334, 336, 337, and 338 were covered with 0.3 c.c. of a 333 ⊙ filtrate, resulting in the formation of  $48 \times 10^4$  plaques of 0.5 m.m. in diameter per c.c. on spreadings of 338b'. A week later they were pasteurized at 90° C. for 10' and then inoculated in 1 % peptone water in ERLNMEYER bulbs. After two days incubation at 30° C. the fluids were filtered and the filtrates tested on the mutilate 338b'. The result was as follows :

Filtrate 334: With a dilution of  $10^{-1}$  no plaques.

Filtrate 336: With a dilution of  $10^{-1}$  no plaques.

Filtrate 337: *With a dilution of  $10^{-3}$  hundreds of plaques with a diameter of 0.5 m.m., 70 % belonging to the ⊙ type, and 30 % to the O type.*

Filtrate 338: *With a dilution of  $10^{-3}$  ten plaques with an average diameter of 0.5 m.m., belonging to the ⊙ type and also to the O type.*

Hence we see in the experiments with the two 333 phages described under C and D that the absorption of both these lytical principles by the

forming spores leads to the presence of the phage in the pasteurized spores. It is very interesting to note that the *megatherium* strains 334 and 336 which could be activated by the 899 phages repeatedly proved to be unsusceptible to the action of 333 phages, whereas strain 338 which repeatedly was found to be unsusceptible to the 899 phages, could be affected by the 333 phages. Strain 337 was susceptible both to the 899 phages and to the 333 phages.

It is worthy of note, moreover, that in the spores the transformation of 333  $\odot$  phage into 333  $\circ$  phage took place to a still greater degree than the transformation of 899  $\odot$  phage into 899  $\circ$  phage. This led me to examine the properties of the 333 phage *in vitro* more carefully than had been done up till now. To my surprise I found that dissemination of 333  $\odot$  phage led to the formation of a majority of  $\odot$  phage plaques, but also to a small but varying number of  $\circ$  plaques, this being contrary to what was found in the case of the 899  $\odot$  phage. Hence it is not necessary in this case to call in the help of the spore to effect the transformation, and although it has not yet been confirmed *in vitro*, it is most probable that the transformation of the 899  $\odot$  phage into the 899  $\circ$  phage may also take place apart from the spore.

Hence since it appeared to be possible that cultures of *megatherium* strains could be so influenced by *megatherium* phages that these strains appeared to possess the power of phage production even after pasteurization, it seemed to me very important to find out whether this power could be communicated to other strains not belonging to the species *megatherium*. To do this young asporogenous cultures of *Bac. undulatus*<sup>1)</sup>, *Bac. mycoides* and *Bac. mesentericus* were treated with a very active *megatherium* lysate in exactly the same way as was done with the *Bac. megatherium*. A week after they had formed spores these cultures were subjected to pasteurization, which would have been destructive to the phage *in vitro*. The filtrate of the culture fluids of these strains was examined in the usual way.

#### E. Experiments with *Bac. undulatus*.

Young vegetative cultures of the *undulatus* strains 1101, 1102, 1106, 1108\*, 1109\*, 1110\*<sup>2)</sup> were treated with 0.3 c.c. of a 899  $\odot$  phage, which formed  $8 \times 10^7$  per c.c. plaques in 338b' spreadings. A week later these cultures were pasteurized at 100° C. for 5', and then inoculated in 1 % peptone water in ERLÉNMEYER bulbs, to which a little of the mutilate 338b' had been added. This was done in case only a very few 899 phage particles should be set free from the above mentioned strains; they would then have the opportunity of multiplying and so be demonstrable. After incubating for two days at 30° C. the contents of the ERLÉNMEYER bottles were filtered and the filtrates obtained tested on 338b' mutilates.

<sup>1)</sup> I have described this bacillus in Zbl. Bakter. I, Orig. Bd. 122 p. 277 (1931).

<sup>2)</sup> The numbers marked with an asterisk produce an undulatus phage.



The result was as follows:

Filtrate 1101:	With a dilution of $10^{-1}$ no plaques.						
Filtrate 1102:	"	"	"	"	"	"	"
Filtrate 1106:	"	"	"	"	"	"	"
Filtrate 1108:	"	"	"	"	"	"	"
Filtrate 1109:	"	"	"	"	"	"	"
Filtrate 1110:	"	"	"	"	"	"	"

The same negative result was obtained after 0.3 c.c. of an 899 O phage had been added.

#### F. Experiments with *Bac. mycoides*.

Young still vegetative cultures of the *mycoides* strains 384, 386, 1161, 1167, 1169 and 1171 were treated with 0.3 cc of a 899 O phage, which led to the formation of  $25 \times 10^6$  plaques per c.c. in 338b' spreadings. A week later these cultures were pasteurized for 10' at 90° C. and then inoculated in 1 % peptone water in ERLNMEYER bottles to which some mutilate 338b' had been added. After two days incubation at 30° C. the contents were filtered and the filtrates tested on the mutilate 338b'. The results were as follows:

Filtrate 384:	With a dilution of $10^{-1}$ no plaques.						
Filtrate 386:	"	"	"	"	"	"	"
Filtrate 1161:	"	"	"	"	"	"	"
Filtrate 1167:	"	"	"	"	"	"	"
Filtrate 1169:	"	"	"	"	"	"	"
Filtrate 1171:	"	"	"	"	"	"	"

The same negative result was obtained after adding 0.3 c.c. of an 899 O phage.

#### G. Experiments with *Bac. mesentericus*.

Young still vegetative cultures of the *mesentericus* strains 999, 1076, 1082, and 1083 were treated with 0.3 c.c. of a 899 O phage, which led to the formation of  $26 \times 10^8$  plaques per c.c. in 338b' spreading. A week later these cultures were pasteurized of 5' at 90° C. and then inoculated in 1 % peptone water in ERLNMEYER bottles to which some of the mutilate 338b' had been added. After 2 days incubation at 37° C. they were filtered and the filtrates obtained tested on the mutilate 338b'.

The result was as follows:

Filtrate 999:	With a dilution of $10^{-1}$ no plaques.						
Filtrate 1076:	"	"	"	"	"	"	"
Filtrate 1082:	"	"	"	"	"	"	"
Filtrate 1083:	"	"	"	"	"	"	"

The same negative result was obtained after 0.3 c.c. of a 899 O phage had been added.

The results of the experiments described under *E*, *F* and *G* show that the spores of *Bac. undulatus*, *Bac. mycoides* and *Bac. mesentericus* when treated with a *megatherium* phage, contrary to the spores of *Bac. megatherium*, never lead to the formation of cultures containing this phage. We may point out that this result is not contrary to what COWLES found seeing he worked with the homologous phages of these bacilli.

Considering too the fact that even a *megatherium* phage is not able to "infect" all *megatherium* spores, it is highly probable that the influence of a certain bacteriophage on certain spores which we have found by experiment to be present, cannot be explained simply by an inclusion during which there is protection against heat of an ultra microbe by the spores, as formely might be thought possible. The influence found to exist can more reasonably be attributed to an induction phenomenon, i.e. the stimulation to perceptible activity of a latent power of phage production in the spores, by the presence of a specific bacteriophage, i.e. one adapted to act upon the same species of spore forming bacillus.

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